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ON THE
STATE OF EQUILIBRIUM
OF CERTAIN
DOUBLE IODIDES, CYANIDES, NITRATES, AND SULPHATES
IN
AQUEOUS SOLUTION.

DISSERTATION
SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

---BY---

BENJAMIN PALMER CALDWELL.

1801..

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Acknowledgment.

I take this opportunity of expressing the pleasure I have enjoyed and the profit I have derived from coming in personal contact with Professor Osa Remsen while under his instruction. The investigation was suggested by Mr. H. C. Jones and was carried out under his supervision. The interest he has shown in its progress and the experimental aid he has given have hastened its completion. My thanks are also due Professor Joseph S. Ames for instruction received from him.

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What is meant by the term double salt ? In the work which is here described the salts employed were those in which different metals were at the same time united with a common acid radicle. There is, however, no intention of limiting the term to that meaning.

(1) Ortwald, Zeitschr. f. ph. Ch. 3, 599.

"Double salts" are supposed to break down immediately into their constituents, and are formed only on the instant of crystallizing from solution.

A sharp line of distinction cannot, however, be drawn between these classes. If we take as an example of a "complex salt" the double cyanide of potassium and nickel,

$K_2 Ni (CN)_4$, we notice the absence of the green color characteristic of solution of nickel salts. Furthermore, certain reactions characteristic of the nickel ion do not take place with this salt.

On the other hand, the double sulphate of potassium and copper,

$K_2 SO_4 \cdot Cu SO_4 \cdot 6 H_2 O$, has a blue color and gives the characteristic reaction of the copper ion. This belongs to the class of

"double salts." But suppose the green color were present in the first case, that fact alone would not tell us that no salt of complex acid existed in solution, and, to continue along the same line of reasoning, the fact of the blue color in the second case does not tell us that all the copper is present as the simple copper ion or in the simple $Cu SO_4$ molecule. There are, therefore, all gradations between "complex" and "double salts." There is good reason for believing that in many instances of double salts, although there is a large proportion decomposed into the constituents, which then dissociate in their usual way, there is still

a portion existing in solution as double salt,.

Diffusion investigations.----Graham⁽¹⁾, in his noted studies on diffusion phenomena, did not limit himself to simple salts, but took ^{up} also a few double salts. He worked on acid potassium sulphate, the double sulphate of potassium and magnesium, and potassium alum. His results seemed to indicate to him that the acid sulphate is decomposed in solution into potassium sulphate and sulphuric acid ; and in the case of the alum also the molecules are broken down, the sulphuric acid, in the one case, and the sulphate of potassium, in the other, being present in the diffusate in larger proportion than they are present in the double salt.

His experiments with the double sulphate of potassium and magnesium were not altogether conclusive. He diffused the double salt and simultaneously in other cells the single constituents. The amount of the double salt diffused was greater than the sum of the amounts of single salts diffused. Hence he presumed that the mixed salts were not combined, and that the double sulphate of magnesium and potassium is not necessarily formed immediately upon dissolving together its constituent salts. Similar results were obtained with the double sulphate of copper and

(1) Graham, Phil. Trans. 1850, 1.

potassium, and its constituents. These double salts appear to dissolve in water without decomposition, although the single salts may come in contact in solution without combining. Hence in two solutions of the same concentration there may be possible more than one state of equilibrium. This view is particularly interesting in connection with some results recorded in this investigation, as will be seen later.

Graham's experiments on double salts were not sufficiently numerous to justify any general conclusion being drawn from them, so the work was taken up and in part repeated by Marignac⁽¹⁾.

Marignac studied the diffusion of salt mixtures such as Ba Cl_2 and Na Cl , $\text{Na}_2 \text{SO}_4$ and Na Cl , K Cl and Ba Cl_2 , and double salts such as $\text{MgSO}_4 \cdot \text{K}_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$, $\text{Mg SO}_4 \cdot \text{Na}_2 \text{SO}_4 \cdot 6 \text{H}_2\text{O}$, etc. His work was very extensive and painstaking, taking into consideration the influence of time, temperature, concentration, relative proportion, etc., on the amount of substance in the diffusate. From the comparison of the simultaneous diffusion of two salts which are capable of forming a double salt, and of those which are not, his results led to the conclusion that solutions of double salts and salt mixtures behave in exactly the same way with regard to diffusion--"whence these results the confirmation of the opin-

(1)

Marignac. Ann. Chim. Phys. (5). 2, 546 (1874).

ion, already established by thermal investigations, that double salts are formed only at the moment of crystallization of their solutions."

This conclusion had been reached previously as a result of the investigations of Vander Wal ⁽¹⁾, who had worked on the diffusion of alum and certain other sulphates.

Ingenhoes ⁽²⁾ reached the same conclusion through the same kind of work. The salts employed by him were barium acetate, calcium acetate-chloride, barium formate-nitrate.

The work of Rüdorff ⁽³⁾ followed this.. He was led to a different opinion and concluded after a very extensive study of double sulphates, chlorides, cyanides, and oxalates that, although a dilute solution of a double salt diffuses in the same manner as if it consisted of the separate constituents, still in concentrated solution a slight difference was to be noted. Double salts, therefore, do exist in solution in an undecomposed condition. The constituents unite to form the double salt, not at the moment of crystallization, but shortly before.

Ortward ⁽⁴⁾ while not disputing results of Rüdorff's work, questioned the validity of his conclusions and suggested to

(1) Van der Wal, Inaugural Diss. Leyden, (1869)..

(2) Ingenhoes, Ber. 12, 1678, (1879).

(3) Rüdorff, Ber. 21, 4 ; 21, 1882 ; 21, 3044 ; 23, 1846.

(4) Ortward, Zeitschr. f. ph. Ch. 3, 60. (1889).

1871

Trevor⁽¹⁾ to undertake some experimental work on the subject of solutions of double salts in water. His method of work was to place in contact with water an excess of a mixture of single salts, and, by means of a pipette provided with a filtering arrangement, to withdraw the liquid at stated times for analysis as to the amount of dissolved substance.

The author criticises Rüdorff's conclusions that in concentrated solution the double salt exists undecomposed. His general conclusion is that double salts, (as defined by Ostwald) exist only in the solid state and not at all in solution. These conclusions do not apply, obviously, to complex salts.

Still later E. Fischer and Schmidner⁽²⁾ in their work on diffusion through rolls of filter paper studied also double salts, such as ferrous ammonium sulphate, etc., and salt mixtures, as potassium and barium chlorides. They reached the conclusion that in dilute solution the double salts are broken down and exist only as their constituents, but on the other hand, in saturated solution the amount of decomposition is so small that it cannot be recognized. This last observation confirms the conclusion of Rüdorff that in thoroughly saturated solution apparently no dissociation takes place.

(1) *Zeitsch. f. ph. Ch.* 7, 468. (1891).

(2) Fischer and Schmidner, *Leibig Ann.* 272, 156 (1892).

Thermal Investigations,---In his Essai de mécanique chimique⁽¹⁾, Berthelot remarks that in the formation of different double salts very different amounts of heat are given off : "In some cases a very considerable amount is evolved, in others a small amount--still, however, approaching that evolved in the formation of a salt of a weak acid." To pull from one of his tables :-

Heat evolved in formation of bisulphate of sodium	8.1.
" " " " " " " potassium	7.5
" " " " " " " biacetate " sodium	0.1
" " " " " " " double sulphate of K & Mg	1.65
" " " " " " " " K & Zn	2.1
" " " " " " " " K & Mn	0.5
" " " " " " " " K & Cu.	0.3
" " " " " " " " cyanide " Hg & K	8.3
" " " " " " " " Ag & K	11.2

He concludes : *But everything indicates* that those salts which are formed with small evolution of heat should be regarded as, in the main, broken down into their constituents by the action of water."

Favre and Valson (2) found that when copper sulphate is

(1) Berthelot, Essai de méch. chim. 1, 366.

(2) Favre and Valson, Comp. rend. 74, 1165, (1872).

dissolved in pure water or in water containing one equivalent of potassium sulphate, the amount of heat liberated is the same. They measured also the amount of heat set free when the sulphuric acid of the double salt is precipitated by barium chloride and found it was equal to that evolved in the precipitation of the constituents separately. They therefore concluded that the double salt experimented upon does not exist in solution undecomposed.

Graham⁽¹⁾ had found that on mixing sulphates which form double salts, no heat is evolved. Even in the formation of alum no certain change was detected. In these cases, however, the double salt formed is less soluble than either of its constituents. He therefore performed the experiment with mercuric chloride and ammonium chloride and noticed the evolution of some heat.

These observations were confirmed by Berthelot⁽²⁾ in his work on the double halides of mercury and of silver. He concluded that mercury and silver could form double salts, (e.g. with potassium) which exist as well in solution as in the solid state. This conclusion based on the fact that the thermal changes brought about on dissolving the double salt were not equal to those in the case of the components.

(1) Graham, Phil. Mag. (3) 20, 539. (1842) ; (3) 24, 401. (1844).

(2) Berthelot, Ann. Chim. phys. (5) 29, 198 (1883).

Investigation on Volume Change.

Kremers (1)

studied the change of volume which occurred on mixing salt solutions, and came to the conclusion that in the cases studied by him, since these changes are so minute there is good ground for the belief that double salts are not formed in solution, but only on the instant of crystallizing out ; and that, therefore, on passing into solution, double salts are immediately broken down into their constituents. His standard of comparison of volume change was that produced by such a vigorous chemical reaction as the neutralization of acids and bases. It is not surprising, therefore, that he considered the volume change produced by the **mixing of the solutions** of salts capable of forming double compounds too minute to indicate chemical reaction.

Favre and Valson (2) also studied the volume changes of double salts and their single constituents. They found that the density of a solution of potassium copper sulphate is the mean of the densities of its constituents, and from this arrived at the same conclusion as that reached by Kremers. Further work in the same line was done by Groshans (3) who came to the same conclusion.

(1) Kremers Pogg. Ann. 98, 58.

(2) Favre and Valson. Comp. rend. 77, 907. (1873).

(3) Groshans, **Des** Dissolutions Aqueuses, 2,7.

Mixing of the solutions

The facts in the case were, on the other hand, brought into question by the investigations of Gerlach. ⁽¹⁾

He did detect on mixing solutions of single constituents of alum, a slight, but appreciable contraction of volume in the case of concentrated solutions. This contraction increased as the dilution was diminished, while as the solutions were made more and more dilute, it gradually vanished. He concluded, therefore, ~~that~~ double salts of this kind are formed and exist, at least partially undecomposed, in concentrated water solution.

Investigations on the solubility of salt mixtures.

The problem of the existence of double salts in solution has been attacked by a number of investigators from this standpoint, and the results obtained have justified their labors.

Kopp ⁽²⁾ announced the following "law" as a result of his work : "Where no chemical reaction takes place between two salts, that one with the stronger base retains its solubility as if the second were not present. The second then dissolves in the solution of the first in proportions which cannot previously be calculated." He considered that there ^{are} two classes of double salts, those which do not retain their compound nature in solution and those which do. He even thinks there may be a new class of

(1) Gerlach, Zeitschr. and Chem. 28, 485. (1839).

(2) Kopp, Liebig's Ann. 34, 260. (1840).

double salts which exist only in solution and which separate into their constituents on removal from solution.

Mulder (1) investigated the influence which the simultaneous presence of two salts may exert on the solubility of individual and on the solubility of double salts. He found that if two or more salts be added to water to saturation, there exists a relation between the quantity of single salts present which indicates the formation of true chemical compounds.

Rüdorff (2) in his studies of the solubility of salt mixtures, came to the same conclusion, but Trevor (3) argues differently.

A number of studies in equilibrium have contributed to the foundation of the idea that, in general, under certain conditions of temperature and concentration, double salts may

(1) Mulder, Bijdragen tot de geschiedenis van het scheikundig gebonden water. Rotterdam, 1864, Jahrb. Ch. 1864, 92; 1866, 65.

(2) Rüdorff, Pogg. Ann. 143, 558. (1873).

(3) Trevor, Zeitschr. f. ph. Ch. 7, 468. (1891).

exist in solution. These investigations (1) can only be mentioned and no attempt can be made to discuss each separately.

(1) Ditte, on the double iodide of lead and potassium.

Ann. Chim. Phys. (5), 24, 226 (1881).

Roozeboom^o astrakanite, ammonium sodium racemate, copper calcium acetate. Zeitschr. f. ph. Ch. 2, 513 (1888) ; 12, 359. (1893)

Meyerhoffer on potassium copper chloride, Zeitschr. f. ph. Ch.

3, 336, (1889).

Vriens on potassium copper chloride, Zeitschr. f. ph. Ch. 7, 194, (1891).

Schreinemaker on potassium lead iodide, Zeitschr. f. ph. Ch. 9, 57. (1892) ; 11, 289. (1893).

Van der Heide on potassium magnesium sulphate, Zeitschr. f. ph.

Ch. 12, 416. (1893).



Certain exceptions had been noted to the principle deduced by Nernst⁽¹⁾ from Van't Hoff's application of the laws of gases to solutions, that if a substance be added to a saturated solution of another salt having a common ion, the solubility of the first is decreased and a part of it precipitated. Le Blanc and Noyes⁽²⁾ examined these exceptions and showed that the apparent discrepancies were due to the formation of double salts in solution.

Work of the same kind had previously been carried out by Rose⁽³⁾ and subsequent work was done by Bodländer⁽⁴⁾ on the solubility of silver halides in ammonia.

Electrolytic Investigations. As early as 1814 Porret⁽⁵⁾ electrolysed potassium ferrocyanide and found that the liquid around the negative pole had an alkaline reaction, while on the positive pole there separated out oxide of iron and hydrocyanic acid. This salt has naturally been the subject of a num-

(1) Nernst, Zeitschr. f. ph. Ch. 4, 372. (1889)

(2) LeBlanc and Noyes, Zeitschr. f. ph. ch. 6, 385. (1890)

(3) Rose, Pogg. Ann. 82, 545, (1851).

(4) Bodländer, Zeitschr. f. ph. ch. 9, 730 (1892).

(5) Porret, Phil. Trans. 1814, 527.

ber of like investigations since that time. The work was repeated and extended by Daniell and Miller ⁽¹⁾.

The classical work in this direction was carried out by Hittorf, ⁽²⁾ who not only electrolysed a number of single salts and first discovered the important principles of electrolytic conduction, but also extended his work to certain double salts such as potassium ferrocyanide, potassium silver cyanide, sodium chlorplatinate, potassium gold chloride, potassium mercury chloride potassium cadmium iodide, and a number of acid salts.

The very names we use to designate some of these compounds viz.: potassium chlorplatinate, tell the result of his work. He found that double salts do exist in solution and ionize into the more positive metal as cation and the acid complex as anion. He firmly established the class of compound now called by Ostwald "complex" salts.

Studies of Electrical conductivity.

A comparatively large amount of work has been done in this

(1) Daniell and Miller, Phil. Trans. 1844, 527.

2 , ; Pogg. Ann. 64, 18, (1845).

(2) Hittorf, Pogg. Ann. 106, 53. (1859).

field. I can only mention the names of a few workers. ⁽¹⁾
 Special mention should perhaps be made of the work of Arrhenius ⁽²⁾
 on isohydric solutions. He showed that although in general the
 amount of dissociation of a substance in solution is altered
 by the addition of another substance, yet no change takes place
 on **the mixing of isohydric solutions**, that is, **of solutions** in
 which the concentration of the common ion per unit volume, is the
 same.

(1) Bouchotte, *Comp. rend.* 62, 955. (1866).

Paalzow, *Pogg. Ann.* 136, 489. (1869).

Svenson, *Beibl.* 2. 46 (1878).

Grotrian, *Wied. Ann.* 18, 177 (1883).

Freund. *Wied. Ann.* 7, 44, (1879).

Bender, *Wied. Ann.* 22, 179, (1884).

Bouty, *Ann. chim. Phys.* (6) 3, 433, (1884) ; 14, 74. (1888).

Croustchaff and Packhoff, *Comp. rend.* 103, 1162. (1889).

Klein, *Wied. Ann.* 27, 151, (1886).

Wershofen, *Zeitschr. f. ph. ch.* 5, 481, (1890).

Kistiakowsky, *Zeitschr. f. ph. ch.* 6, 97, (1890)

(2) Arrhenius, *Beibl.* 9, 437. (1885) ; *Wied. Ann.* 30, 51, (1887)

As a result of all this work it has been firmly established that in the case of complex salts the conductivity is very different from the mean of the conductivities of the constituents and that the complex exists undecomposed in part at least, even in the dilute solutions. In the case of mixtures of electrolytes not capable of forming double salts the difference is smaller.

A special study has been made in this laboratory of the conductivity of double salts which would not ordinarily be classed among the complex salts. Jones and Mackay ⁽¹⁾ studied certain alums and found that the difference between the conductivity of the alums, and the sum of the conductivity of the constituent salts, was greater than that which exists between the conductivity of mixtures of salts not capable of forming double salts, and the sum of their separate conductivities. They concluded that the alums studied are to be classed as true double salts even while in solution. At very great dilution, however, no distinction could be drawn between their behavior and that of a mixture of the constituents.

Somewhat later Jones and Ota ⁽²⁾ extended the work to certain double chlorides and obtained in general the same results.

(1) Jones and Mackay, *Am. Ch. Jr.* 19, 83.

(2) Jones and Ota, *Am. Ch. Jr.* 22, 5.

It was evident however, that these solutions assume the condition of a mixture of the constituent salts at much smaller dilution, that is, the complex ion breaks down into simpler ones much more easily under the influence of increasing dilution than in double sulphates. Jones and Knight ⁽¹⁾ continued the work and investigated the behavior of certain other chlorides and double bromides. As the work here described is an extension of the above to certain double sulphates (not alum), iodides, cyanides, and nitrates, and as the method of work is the same, it need not be detailed here.

Cryoscopic investigations. This line of investigation has been followed to a small extent. Raoult ⁽²⁾ by comparing the depression of the freezing point of water caused by solutions of double salts with the sum of the depressions produced by the constituent salts, concluded that certain salts, as the double chloride of mercury ^{and platinum} do exist undecomposed in solution, but that other salts, as certain double sulphates, are entirely dissociated into their constituents.

Le Blanc and Noyes ⁽³⁾ in their work referred to above

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- (1) Jones & Knight, Ann. Ch. Jr. 22, 110.
 - (2) Raoult, Compt. rend. 99, 914, (1884).
 - (3) Le Blanc & Noyes, loc. cit.

also made use of cryoscopic observations. Some work has also been done by Jones and Mackay⁽¹⁾ and Jones and Ota.⁽²⁾ The method on the whole, while indicating the existence of certain double salts in solution, cannot be said to have proved as satisfactory as that based on the electrical conductivity of the salt solutions.

GRAPHICAL CALCULATIONS. Basing his reasoning on Arrhenius' theory of isohydric solutions, MacGregor⁽³⁾ has deduced certain methods for calculating the conductivity (and other ionic properties) of mixtures of electrolytes which do not act upon one another chemically, from certain data known concerning the single constituents, viz : (a) the quantities present in a given volume of the solution ; (b) their amounts of dissociation ; (c) their molecular conductivities at infinite dilution.

If v is the volume of a certain solution which contains N_1, N_2, N_3, \dots etc. gramme-equivalents of the respective electrolytes present ; if $\alpha_1, \alpha_2, \alpha_3, \dots$ etc. are their respective coefficients of dissociation or ionization, and if

(1) Jones & Mackay, loc. cit.

(2) Jones & Ota, loc. cit.

(3) MacGregor, Trans. N. S. Inst. Sci. 9, 101, 1895-96 ; Phil. Mag. (5), 41, 276, 1896, Trans. Roy. Soc. Can., (2) 2, Sec. 3, 65, 1896-7.

$\mu_{\alpha_1}, \mu_{\alpha_2}, \mu_{\alpha_3}, \dots$ etc. are their respective specific conductivities per gramme-equivalent at infinite dilution, then, according to the above theory, the specific conductivity of the solution is equal to $\frac{1}{V} (d_1 N_1 \mu_{\alpha_1} + d_2 N_2 \mu_{\alpha_2} + d_3 N_3 \mu_{\alpha_3} \dots \text{etc.})$

He then deduced four equations which if graphically employed enable one to calculate the conductivity of mixtures of electrolytes to a high degree of accuracy in dilute solutions. In a mixture of electrolytes each may be considered as occupying its own distinct portion of the solution. If we denote the electrolytes by 1 and 2, the concentrations (in gramme-equivalents per litre) of the solutions with respect to them by N_1 and N_2 , respectively, their ionization coefficients by d_1 and d_2 , and their regional dilutions (in litres per gramme equivalents) by V_1 and V_2 , respectively, then, when the solutions are in equilibrium with respect to each other,

$$\frac{d_1}{V_1} = \frac{d_2}{V_2} \dots \dots \dots (1)$$

that is, the numbers of the free gramme-ions of the electrolytes per unit volume of their respective regions are equal.

$$N_1 V_1 + N_2 V_2 = 1 \dots \dots \dots (2)$$

that is, the volume of the solution is equal to the sum of the volumes of the regions of the respective electrolytes.

$$\frac{d_1}{V_1} = f_1(V_1) \dots \dots \dots (3)$$

$$\frac{d_2}{V_2} = f_2(V_2) \dots \dots \dots (4)$$

that is, the regional ionic concentrations are functions of the respective regional dilutions.

By means of curves plotted these relations are worked out more easily than by pure mathematics, and the estimation of the conductivity of mixtures at different dilutions can be accurately made. In testing MacGregor's graphical method the work of his students ⁽¹⁾ has shown that in dilute solutions it holds accurately, but that in more concentrated solutions, where the ~~of~~ of the constituent salts cannot be considered the same (due to the presence of a large quantity of another salt) as when ~~water~~ alone is the solvent, discrepancies arise.

It would seem, then, as a general result of the foregoing historical survey of the investigations that have been made on the subject of double salts in solution, that, so far as dilute solutions are concerned, Ostwald's distinction between complex and

(1) McINTOSH, Trans. N. S. Inst. Sci., 9, 120, 1895-6 ; Phil. Mag. (5)

41, 510, 1896.

Archibald, Trans. N. S. Inst. Sci. 9, 291, 307, 335 ; Trans. Roy. Soc. Can. (2), 3, Sec. III, 69, 1897-8.

McKay, Trans. N. S. Inst. Sci. 9, 321, 1897-8.

double salts can be sharply drawn. Those salts which exhibit in dilute solution different properties from those of its constituents, do also on electrolysis show a complex anion. But, in concentrated solution, certain other salts show these differences, and it is fairly certain that the nature of their complex ions, or indeed their existence, cannot be directly demonstrated by electrolysis.

The present work has been undertaken to gain further knowledge in order that if possible the classification may be more definitely made. The work has ~~been~~ embraced the study of certain double sulphates which are not alums, certain double nitrates and iodides, and a double cyanide. The work has consisted of a comparison of the electrical conductivity of the double salts with that of their constituents salts. Some cryoscopic work has also been done.

APPARATUS.

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The apparatus employed in the measurement of the electrical conductivity of the solutions was that devised by Kohlrausch and improved and described by Ostwald.⁽¹⁾ It consisted of a Wheatstone's bridge, telephone, induction coil, resistance box, cell, and thermostat.

(1) Ostwald. Zeitsch. f. ph. 6n. 2, 561, (1888).

The bridge consisted of a "Manganine" wire one metre long running beside a millimetre scale. Readings were in general confined by means of suitable resistance to the space between 400 and 600 on the scale, since the ratio $\frac{a}{1000-a}$ is more accurately obtained when a equal 500 than when it equals, e.g. 100 or 900.. By employing ~~three~~ different resistances three readings were made on each solution. The results recorded are the mean of these. The telephone used was what is known as the "watch-case" style, and gave good tones and minima with the induction coil employed.

The induction coil was made to order by M. E. Leeds & Co., Phila., and gave the greatest satisfaction throughout the work. By a system of very thick, rigid steel bars carrying the "make-and-break" spring, the tone obtained was of exceptionally high pitch. The whole was encased in a box with the connections leading to binding posts on the outside. The screw for the adjustment of the spark-gap was controlled from the exterior. The tone given in the telephone was continuous, and the action of the coil so silent that it could easily have been used on the same desk with the bridge, but for convenience was placed at a distance of ~~about~~ eighteen feet away. The coil was operated by a storage cell giving about two volts.

The resistance box contained 11110.5 Ohms in individual coils, ranging from 4000 ohms down to 0.5 ohms. The box was certified as accurate to $1/25$ of one per cent.

The thermostat was of the usual form, containing about 20 litres of water kept in circulation by a stirrer operated by a hot air fan. The cell rested on a hard rubber shelf and contact was made with the wires leading there permanently through small mercury cups. The temperature of the bath was kept constant by means of an Ostwald gas regulator.

The thermometer employed was one graduated in tenths of a degree and tested correct.

The cells used were of the Arrhenius type. Two cells were employed, one with the electrodes close together for dilute solution, and the other with electrodes far apart--for concentrated solutions. These cells were frequently restandardized with $\frac{N}{50}$ K Cl ($\mu_{25^\circ} = 1297$) and a check was kept on the standardizations by determining with every substance the conductivity of some solution in both cells.

All graduated vessels used in making up solutions, such as flasks, pipettes, and burettes were calibrated by the method of Morse & Blalock.⁽¹⁾

SOLUTIONS.

The constituents of the double salts were in every

(1) Morse and Blalock Am. Ch. Jr. 18, 479.

case the c. p. article from such firms as Bender and Hobein of Dresden, Theodor Schuchart, of Görlitz, or Einer and Amend, New York. These were purified in every case by recrystallization and tested as to purity by analysis. The double salts were made by bringing together the proper amount of the constituents, and dissolving the whole mixture. They were then crystallized out slowly, care being taken to prevent too rapid a deposit of crystals.. The solutions were never evaporated to such a degree as to remove anything like the whole amount of dissolved substance. The crystals were rapidly freed from the mother-liquor, and where the great solubility of the salt did not prevent, were washed with water. After drying on absorbent paper they were analyzed. All the sulphates were treated in this way; the cyanides, iodides and nitrates did not permit of washing.

The single constituents and double salts were dissolved in pure water and mother-solutions of convenient strength were prepared and analyzed. From these suitable dilutions were made. Two methods of diluting were employed. In some cases fifty cubic centimeters of the solution were measured into the conductivity cell, and after its conductivity had been determined twenty-five cubic centimetres were withdrawn by means of a pipette and the same amount of water added, in cases where it was wished to double

the volume of the solution. In this way dilutions were made in the cell from a solution of volume 1 to volume 2, to volume 4, to volume 8, to volume 20. A solution of volume 20 was then made from the original solution directly in a measuring flask and its conductivity was compared with that of the solution made by successive dilutions in the cell. Very small differences were noted, and the proportional corrections ⁽¹⁾ were applied to the solutions previously made. This latter solution was then diluted in the cell three or four times, and the conductivity of the last ~~solution~~ was compared with one of the same concentration made directly from the original mother-solution.

The other method of diluting was the simple one of making each dilution directly from the mother-solution. For example, from a solution of volume 1, solutions of volume 2, 4, 8, 20, 40 would be prepared in measuring flasks. Further dilution would then be made from the last (40) as a mother-solution.

It has been argued in favor of the first method that time is saved. I am of the opinion that not only is the second method more accurate, but it does not require any more time.

All the water used in making up solutions and washing out apparatus was purified by distillation in the manner described by Jones and Mackay⁽²⁾. Corrections were applied to the conduc-

(1) Kohlrausch, Wied. Ann. 26, 134, (1835).

(2) Jones & Mackay, Zeitschr f. ph. Ch. 22, 237; Am. Ch. Jr. 19, 91

dilute solutions - Effect of the

tivity of the _A water being determined for each substance worked upon. The conductivity of the water ranged from 1.1×10^{-3} up to occasionally 3.0×10^{-3} reciprocal ohms. All water was preserved in vessels which had been used alone for that purpose for a number of years.

In the work which is detailed below all the solutions were made upon the basis of the molecular weight of the substance. A solution of volume 1 contains one gramme-molecular-weight of the substance dissolved in a litre of water. The symbol ν is used to denote the number of litres of the solution which contain one gramme-molecular weight of the substance. The symbol μ_{ν} is used to denote the specific molecular conductivity of the solution at the volume ν . The column marked "Concentration" in the tables that follow contains the strength of the solution in terms of one gramme-molecule per litre as normal. In the cryoscopic work the symbol L is used to denote the actual depression of the freezing point of the solvent by the dissolved substance and Δ , the molecular lowering.



DOUBLE IODIDES.

Double Iodide of Potassium and Cadmium.

The conductivity of cadmium iodide has been determined by Grotrian and Wershofen (1) and I have interpolated between their values.

I. Cadmium Iodide, Cd I_2 . Molec. wt. 365.70

v	$\mu_{v, 18^\circ}$	
1		
2	28.2	
4	34.0	
10	43.8	
20	55.6	
40	73.4	
100	99.6	
200	121.8	
400	143.4	
1000	171.8	
2000	183.2	

(1) Grotrian and Wershofen-Wied. Ann., 18, 177. (1883) and Zeitschr. f. pt. Ch. 5, 481. (1890).

The conductivity of potassium iodide has been determined by Kohlrausch (1), and I have interpolated between his values.

II. Potassium Iodide, KI. Molec.wt. 166.0.

v	κ_v 180	$2/\kappa_v$ 180	
1	96.8	193.6	
2	99.7	199.4	
5	102.4	204.8	
10	106.9	213.8	
20	110.2	220.4	
50	113.2	226.4	
100	116.1	232.2	
200	118.3	236.6	
500	119.7	239.4	
1000	120.3	240.6	
2000	121.2	242.4	

(1)

Kohlrausch, Wied. Ann. 26. 161 (1885)

The conductivity of the double iodide of Potassium and cadmium has been determined by Grotrian and Wershofen (1).

III.

Potassium Cadmium Iodide. K_2CdI_4 . Molec. wt. 697.70

V	μ_{v180}	
2	151.6	
4	166.0	
10	188.0	
20	208.0	
40	228.8	
100	285.4	
200	313.0	
400	344.8	
1000	378.0	
2000	401.0	
4000	408.0	

(1)

Grotrian and Wershofen loc. cit.

The comparison of the conductivity of the double salt with the sum of the conductivities of the constituent salts must be made so as to take into account the fact that two molecules of potassium iodide are present in the double salt to every one of the cadmium iodide. Twice the conductivity of the potassium iodide at one-half the dilution of the cadmium iodide is added to the conductivity of the latter, and the sum is compared with that of the double salt at the latter volume.

IV. Comparison. Cadmium Potassium Iodide.

V	$2\mu_{V/180} KI.$	V	$\mu_{V/180} CdI_2$	Sum	$\mu_{V/180} K_2 Cd I_4$	Difference
1	193.6	2	28.2	221.8	151.6	70.2
2	199.4	4	34.0	233.4	166.0	67.4
5	204.8	10	43.8	248.6	188.0	60.6
10	213.8	20	55.6	269.4	208.0	61.4
20	220.4	40	73.4	293.8	228.8	65.8
50	226.4	100	99.6	326.0	285.4	40.6
100	232.2	200	121.3	354.0	313.0	41.0
200	236.6	400	143.4	380.0	344.8	35.2
500	239.4	1000	171.8	411.2	378.0	33.2
1000	240.6	2000	183.2	423.8	401.0	22.8
2000	242.4	4000	-	-	408.0	-

DOUBLE IODIDE OF CADMIUM AND STRONTIUM.

The salt was prepared by dissolving together the amounts of pure cadmium iodide and strontium iodide required to make a double salt containing one molecule of each constituent. The double salt crystallizes out easily although it is quite soluble. It has the composition $\text{Cd Sr I}_4 \cdot 8\text{H}_2\text{O}$.

ANALYSIS. The cadmium was precipitated from the acidified solution with hydrogen sulphide and the strontium, after expulsion of the sulphuretted hydrogen, was determined in the filtrate by precipitation with sodium carbonate. The cadmium sulphide precipitate was collected in a Gooch crucible and was washed with chloroform and carbon bisulphide to remove any precipitated sulphur.

I. 2.2325 gr. crystallized salt gave 0.3950 gr. CdS and 0.3795 gr. Sr CO_3 .

II. 1.9053 gr crystallized salt gave 0.3285 gr Sr CO_3 ,
calculated for $\text{CdI}_2 \cdot \text{Sr I}_2 \cdot 8\text{H}_2\text{O}$:-

	I.	II.	
Found,	13.75	—	% Cd.

Theoretical, 13.17 % Cd.

	I.	II.	
Found,	10.08	10.23	% Sr

Theoretical, 10.17 % Sr.

The iodine was determined by titration of the solution against N/10 silver nitrate.

Dissolved 0.9942 gr. crystallized salt in 100 c.c. water.

25 cc solution were equivalent to 10.34 cc

" " " " " " 10.38 cc

mean 10.36 cc AgNO_3 , $N \times 0.11255$.

Found, 59.50 % iodine

Theoretical, 59.61 % iodine.

PREPARATION OF THE SOLUTION:- The salt was weighed out approximately so as to make a normal solution when dissolved in a litre of water. A portion of the solution was diluted twenty times and ten c.c. portions were titrated against silver nitrate solution.

10 cc were equivalent to 17.85 cc

" " " " " 17.89 cc

mean 17.87 cc AgNO_3 , $N \times 0.11255$.

The original solution therefor had a concentration $N \times 0.9944$ and its volume was 1.0056.

Conductivity of the double iodide of cadmium and strontium:-

V. Cadmium. Strontium Iodide $\text{Cd Sr I}_4 \cdot 8\text{H}_2\text{O}$. Molec wt. 846.39

v	Concentration.	Gr. cryst. salt per Litre.	μ_v 25o	
1.0056	0. 9944	846.39	91.1	
2.0112	0. 4972	423.19	121.9	
4.0224	0. 2486	211.59	144.4	

10.056	0. 09944	84.639	172.5
20.112	0. 04972	42.319	199.9
40.224	0. 02486	21.159	235.4
100.56	0.009944	8.4639	289.1
201.12	0.004972	4.2319	324.4
402.24	0.002486	2.1159	357.6
1005.6	0.000994	0.8464	393.2
2011.2	0.000497	0.4232	426.4
4022.4	0.00025	0.2116	454.5
10056	0.0001	0.0846	462.6

Conductivity of Cd Sr I_4 calculated for even volumes.

VI.

Cd Sr I_4

v	$\mu_{v, 25^\circ}$	v	$\mu_{v, 25^\circ}$	v	$\mu_{v, 25^\circ}$
1	90.93	20	199.82	400	357.6
2	121.58	40	235.05	800	393.2
4	144.17	80	270.84	2000	426.4
8	162.89	200	324.39	4000	454.5

STRONTIUM IODIDE.

The salt was purified by crystallization and analyzed for purity.

3.413 gr crystallized salt were dissolved in 1000 c.c. water and 10 c.c. portion were titrated against silver nitrate, N X O. 11255.

10 cc solution were equivalent to 14.40 cc

10 cc " " " " 14.41 cc

Found 60.25 % iodine

Calculated for $\text{Sr I}_2 \cdot 6\text{H}_2\text{O}$, theoretical % I. 51.98.

The solution for the determination of the conductivity was made up and standardized by precipitating the strontium as carbonate. Ten c.c. of the solution were diluted to one hundred, and ten c.c. portions were taken for precipitation.

	I.	II.
Wt. SrCO_3	0.1168 gr.	0.1167 gr.

The solution had a concentration N X O. 78 29, and its volume was 1.2644.

CONDUCTIVITY OF STRONTIUM IODIDE.

VII. Strontium Iodide, SrI_2 . Molec. Wt. (cryst) 449.42				
v	Concentration	Gv. Cryst. : salt per Litre.	:	$\mu_{v, 25^\circ}$
1.2644	0.7829	351.85		150.56
2.5288	0.3914	175.92		169.29
5.0576	0.1957	87.96		181.77
12.644	0.07829	35.18		196.79
25.288	0.03914	17.59		206.04
50.576	0.01957	8.79		217.83
126.44	0.007829	3.518		229.82
252.88	0.003914	1.7592		239.12
505.76	0.001957	0.8796		245.59
1264.4	0.000729	0.3518		248.58
2528.8	0.000391	0.1759		253.89

Conductivity of SrI_2 calculated for even volumes.

VIII. SrI_2					
v	$\mu_{v, 25^\circ}$	v	$\mu_{v, 25^\circ}$	v	$\mu_{v, 25^\circ}$
1	146.65	20	202.18	400	242.84
2	161.45	40	212.97	800	247.19
4	176.56	80	222.24	2000	251.78
8	187.59	200	235.40		

The conductivity of cadmium iodide is given above.

IX. Comparison. Cadmium Strontium Iodide.

v	$\mu_{iv} 250 \text{ SrI}_2$	$\mu_{iv} 250 \text{ CdI}_2$	Sum	$\mu_{iv} 250 \text{ SrCdI}_4$	Difference
1	146.65	-	-	90.93	-
2	161.45	28.2	189.6	121.58	68.0
4	176.56	34.0	210.56	144.17	66.4
8	187.59	40.6	228.2	162.89	65.3
20	202.18	55.6	257.8	199.82	58.0
40	212.97	73.4	286.4	235.05	51.4
80	222.24	91.0	313.2	270.84	42.4
200	235.40	121.8	357.2	324.29	32.9
400	242.84	143.4	386.2	357.59	28.6
800	247.19	162.4	409.6	381.2	28.4
2000	251.78	183.2	435.0	426.38	8.6

DOUBLE CYANIDE OF POTASSIUM AND MERCURY.

This salt was obtained by crystallizing from a solution containing the constituent salts in the proportion to form $\text{Hg}(\text{CN})_2 \cdot 2\text{KCN}$.

ANALYSIS:- The mercury was precipitated as mercuric sulphide and was collected and weighed in a Gooch crucible. The precipitate was washed with carbon bisulphide to remove any excess of sulphur that might have been present. The salt is very hygroscopic and the crystals taken for analysis were only dried on absorbent paper.

I. 1.3529 gr. salt gave 0.8025 gr. Hg 5.

II. 1.4593 gr. salt gave 0.8641 gr. Hg 5.

Theoretical Hg in $\text{Hg}(\text{CN})_2 \cdot 2\text{KCN}$ 52.33 %

Found Hg in $\text{Hg}(\text{CN})_2 \cdot 2\text{KCN}$ (I. 51.13 %
(II. 51.04 %

As the substances employed had been previously recrystallized a number of times, and as the crystals of double salt were well formed and, furthermore, since the substance used for analysis had been only dried on absorbent paper, the analysis was taken to indicate pure double salt, and it was used without further recrystallization for the purposes of the investigation.

The solution prepared for the determination of the electrical conductivity was analysed in the same way.

I. 4 cc. solution gave 0.7617 gr. HgS .

II. 4 cc. solution gave 0.7610 gr. HgS .

The solution was, therefore, N X 0.8191 and its volume 1.2210. It contained 313.5187 grs. to the litre.

Conductivity of the double cyanide of potassium and mercury:-

				Molec.wt.
X.	Potassium	Mercury Cyanide: $\text{Hg}(\text{CN})_2$	2 KCN.	382.76
v	Concentration	Grms. per Litre	μ 25°	
1.221	0.8191	313.5187	155.0	
2.442	0.4095	156.7593	173.1	
4.884	0.2047	78.3796	186.8	
12.21	0.08191	31.3518	202.0	
24.42	0.04095	15.6759	211.53	
48.84	0.02047	7.8379	222.0	
122.1	0.008191	3.1352	234.0	
244.2	0.004095	1.5676	240.0	
488.4	0.002047	0.7838	244.3	
1221.0	0.000819	0.3135	248.9	
2442.0	0.000409	0.1567	251.2	
4884.0	0.000204	0.0784	259.5	
12210.0	0.000082	0.0313	258.8	

Conductivity of $K_2Hg(CN)_4$ calculated for even volumes.

XI. $K_2Hg(CN)_4$						
v	μ_v 250	v	μ_v 250	v	μ_v 250	
2	166.5	40	117.9	800	245.6	
4	181.8	80	227.1	2000	250.4	
8	193.3	200	237.8			
20	208.1	400	242.8			

MERCURIC CYANIDE.

ANALYSIS:-

- I. 5 cc. solution gave 0.4660 gr Hg S.
 II. 5 cc. solution gave 0.4659 gr Hg S.

The solution therefore had a concentration $N_{\lambda}0.4013$, and its volume was 2.4937.

It contained 101.28 grs. to the litre.

The conductivity of this substance is very small, so that only the most concentrated solutions gave distinct readings on the Wheatstone's bridge.

Conductivity of Mercuric Cyanide:-

XII. $Hg(CN)_2$ Molec.Wt.252.38			
v	Concentration	Grs. per Litre	μ_v 250
2.4937	0.4013	101.28	0.2775
4.9874	0.2006	50.64	0.2957
9.9748	0.1003	25.32	0.3198
24.937	0.0401	10.13	0.3787

Conductivity of mercuric cyanide calculated for even volumes:-

XIII.		Hg (CN) ₂ .
v	$\mu_{v \ 250}$	
4	0.2884	
8	0.3104	
20	0.3588	

POTASSIUM CYANIDE.

ANALYSIS OF SOLUTION:-

- I. 5 c.c. solution gave 0.6079 gr K₂SO₄.
- II. 5 c.c. solution gave 0.6083 gr K₂SO₄.

The solution was therefore, Nx 1.3944 and its volume 0.7171. The solution contained 90.9009 grs. to the litre.

Conductivity of potassium cyanide:-

XIV.		Potassium Cyanide. KCN.	Molec.wt. 65.19	
v	Concentration	Grs. per Litre	$\mu_{v \ 250}$	
0.7171	1.3944	90.9009	110.69	
1.4342	0.6972	45.4504	119.74	
2.8684	0.3486	22.7252	126.71	
7.171	0.1394	9.0900	133.20	
14.342	0.0697	4.5450	138.88	
28.684	0.0348	2.2725	144.76	

71.71	0.0139	0.9090	150.38
143.42	0.0069	0.4545	154.98
286.84	0.0035	0.2272	157.98
717.1	0.0014	0.0909	162.30

Conductivity of potassium cyanide calculated for even volumes.

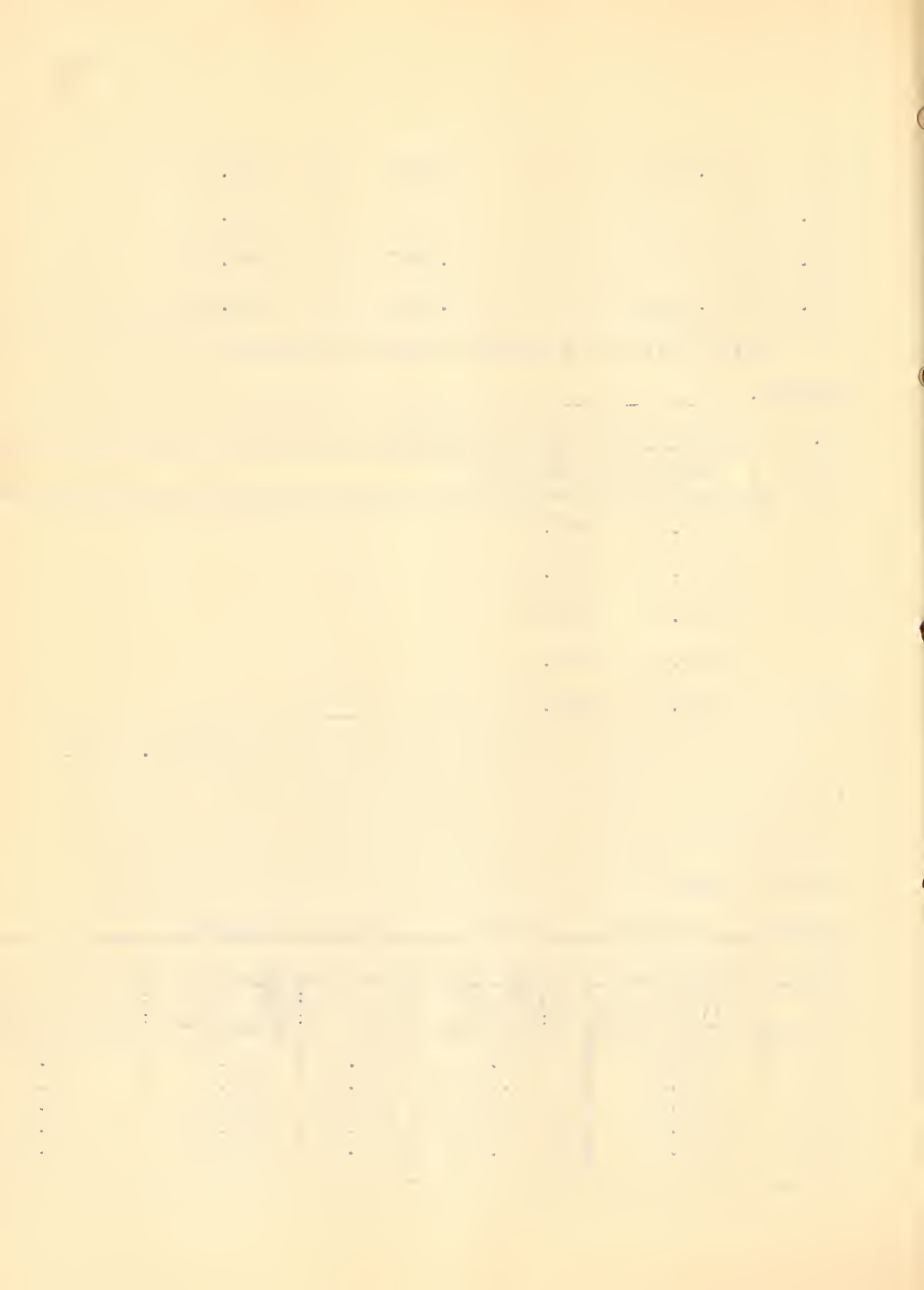
XV. Potassium Cyanide. KCN.

v	$\mu_{IV} 25^{\circ}$	$2\mu_{IV} 25^{\circ}$
1	114.26	228.52
2	122.49	244.98
4	128.41	256.82
10	135.43	270.86
20	141.20	282.40

Since the double salt has the composition $\text{Hg}(\text{CN})_2 \cdot 2\text{KCN}$, in making the comparison of its conductivity with the sum of the conductivities of the constituent salts, that of the potassium cyanide must be taken at one-half the dilution and doubled. The case is parallel to that of $\text{CdI}_2 \cdot 2\text{KI}$.

XVI. Comparison. Mercury Potassium Cyanide.

v	$2\mu_{IV} 25^{\circ} \text{KCN}$	v	$\mu_{IV} 25^{\circ} \text{Hg}(\text{CN})_2$:Sum	$\mu_{IV} 25^{\circ} \text{HgK}_2(\text{CN})_4$	Difference
1	228.52	2	(0.25)	228.77	166.5	62.2
2	244.98	4	0.2884	245.27	181.8	63.4
4	256.82	8	0.3104	257.13	193.3	63.8
10	270.86	20	0.3588	271.22	208.1	63.1
20	282.40	40	(0.39)	282.79	217.9	64.9



The results obtained with the above double iodides and the cyanide indicate that these salts exist in solution undecomposed into their constituents, in part at least, even up to and over a dilution of 2000. The "difference" in the case of the double iodide of cadmium and potassium at a volume of 1 amounts to 31 % of the sum of the conductivities of the constituents. In the case of the double iodide of cadmium and strontium it amounts to 35 % at a volume 2, and in the case of the double cyanide of mercury and potassium it amounts to 27 % at a volume 1.

(1)
Jones and Knight found that the "difference" in the case of the double chloride $2\text{NaCl} \cdot \text{Zn Cl}_2$, and $5\text{r Cl}_2 \cdot 2\text{Cd Cl}_2$, amounted to 35-45 % for concentrated solutions, and that these differences persisted even at a higher dilution than 9000 litres; while in the case of mixtures of chlorides which are not capable of forming double salts such as $\text{KCl} + \text{NH}_4\text{Cl}$ and $\text{KCl} + 2\text{NE}_4\text{Cl}$, it amounted only to 11-14 %, and entirely disappeared at about 500 litres.

No very complete information is obtainable as to the behavior of mixtures of iodides. The magnitude of their conductivity is not very different from that of the chlorides, however, and we are justified by the well known similarity of the behavior of halogen salts in general, in making the com-

(1) Jones and Knight, loc.cit.



parison with them. Such a comparison indicates without doubt that the iodides under consideration are not completely dissociated in solution. They also, like the chlorides studied by Jones and Knight(1) and Jones and Ota(2), retain their compound character to high dilutions. We are not quite as fully justified in making the comparison of the cyanide with the chlorides, but, were we to do so, the same conclusion would be reached in regard to them as in the case of the chlorides and iodides.

A comparison with the differences shown by mixtures of bromides which do not combine to form double salts strengthens the above conclusion. They behave entirely like the chlorides and there is no reason for supposing that the iodides conduct themselves differently. Direct experimental proof would, however, be desirable.

In their paper referred to above Cronstchoff and Packhoff(1) give some meagre information on the deportment of solutions of mixed halides. They find that the conductivity of the solution $1/2$ ($\text{NaBr} + \text{KI}$) actually observed is about 1% smaller than that calculated from the conductivities of the constituents. The difference in the case of the solu-

(1) Jones and Knight, loc.cit.

(2) Jones and Ota, loc.cit.

(1) Cronstchoff and Packhoff, loc.cit.

tion $1/2$ (NaI + KBr) is given as about $3-1/2$ %, while that in the case of $1/2$ (KI + NaI) is about $1/2$ %. This is the only direct experimental evidence we possess on the conductivity of mixtures of iodides and makes clear the fact of the existence of these double iodides in concentrated solution.

DOUBLE NITRATES.

Double Nitrate of Ammonium and Praseodymium.

It was deemed desirable to investigate the condition of double nitrates in solution. Very few double nitrates exist, however, where both constituents are soluble in water. I was fortunate in having at my disposal a fairly good quantity of praseodymium^{and neodymium} nitrates and oxides which were in a high state of purity, having been repeatedly crystallized in the course of an investigation carried on some time ago in this laboratory(1) on the atomic weights of praseodymium and neodymium.

In the case of praseodymium the substances at my disposal were praseodymium nitrate and the double nitrate of praseodymium and ammonium. The method used for the purification of the substances employed, as well as their degree of purity are recorded in the article mentioned.

(1) Jones, Am. Ch. Jr. 20, 345.



Solutions were prepared and standardized by the determination of the praseodymium. This was precipitated with ammonium hydroxide and the precipitate was ignited to oxide in a porcelain boat. This oxide has the formula Pr_4O_7 . As there is some doubt as to whether the oxide has a definite composition the precipitate was ignited in a rapid stream of hydrogen, purified by passing through lead plumbate and sulphuric acid, and reduced to the well known compound Pr_2O_3 .

The loss in weight on ignition in hydrogen and the equal gain in weight on subsequent ignition in air convinces me that the oxide Pr_4O_7 does exist, and can just as safely be used in the analysis of praseodymium salts as the lower oxide, Pr_2O_3 .

Analysis of solution of double nitrate of Praseodymium and Ammonium:-

- I. 2 c.c. solution gave 0.3944 gr. Pr_2O_3 .
 II. 2 c.c. solution gave 0.3968 gr. Pr_2O_3 .

The concentration of the solution was, therefore, $\text{N} \times 1.2072$, and its volume 0.8314. It contained 568.40 gr. of the anhydrous salt, $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3$.

Conductivity of the double salt:-

				Molec.wt
XVII. Ammonium Praseodymium Nitrate $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3$				486.82
v	Concentration.	Gms. per Litre.	μ_v 250	
0.8314	1.2027	568.40	134.1	
1.6628	0.6013	284.20	248.0	

3.3256	0.3006	142.10	334.9
8.314	0.1203	56.84	404.7
16.628	0.0613	28.42	451.1
33.256	0.03006	14.21	491.1
83.14	0.01203	5.684	531.3
166.28	0.006013	2.842	555.8
332.56	0.003006	1.421	550.3
831.8	0.001202	0.5634	613.2
1662.8	0.000601	0.2842	628.0
3325.6	0.000300	0.1421	642.8
8314.0	0.000120	0.0568	654.3

The conductivity of praseodymium ammonium nitrate calculated for even volumes:-

XVIII. $\text{Pr}(\text{NO}_3)_3 - 2\text{NH}_4\text{NO}_3$

ν	$\mu_{\nu 25^\circ}$	ν	$\mu_{\nu 25^\circ}$	ν	$\mu_{\nu 25^\circ}$
1	157.0	20	459.2	400	585.0
2	265.6	40	496.5	800	604.0
4	344.3	80	528.8	1000	608.8
8	400.2	100	536.3	2000	631.0
10	413.9	200	560.8	4000	644.3

PRASEODYMIUM NITRATE.

This was made from the oxide by treatment with nitric acid and repeated (eight to ten times) evaporation to crystallization to remove the excess of acid.

The solution was analyzed in the same way as the double salt.

- I. 10 cc original solution₄ gave 0.1586 gr. Pr_2O_3 .
 II. 10 cc original₄solution gave 0.1586 gr. Pr_2O_3 .

The volume of the solution was therefore 2.6305 and its concentration 0.38015. It contained 124.15 grs. of the anhydrous salt to the litre.

Conductivity of praseodymium nitrate:-

XIX. Praseodymium Nitrate. $\text{Pr}(\text{NO}_3)_3$. Molec. Wt. 326.58

ν	Concentration.	Grms. per Litre.	$\mu_{\nu} 25^\circ$
2.6305	0.38015	124.15	153.9
5.2610	0.19007	62.07	186.4
10.5220	0.09503	31.03	213.9
21.0440	0.04751	15.51	239.3
52.610	0.01900	6.207	270.9
105.22	0.00950	3.103	289.7
210.44	0.004751	1.551	308.2
526.1	0.001900	0.6207	336.4
1052.2	0.000950	0.3103	346.5

2104.4	0.000475	0.1551	359.7
5261.0	0.000190	0.06207	374.0
10522.0	0.000095	0.63103	396.0

Conductivity of praseodymium nitrate calculated for
even volumes:-

XX. Praseodymium Nitrate.

✓	μ_v 25°	✓	μ_v 25°	✓	μ_v 25°
2	146.0	40	258.3	800	341.8
4	170.9	80	280.9	1000	345.9
8	200.8	100	288.6	2000	359.3
10	213.9	200	308.4	4000	370.6
20	236.8	400	325.2		

AMMONIUM NITRATE.

The substance used had been repeatedly crystallized,
then dried to constant weight. The solution was then made
up by weight.

Conductivity of Ammonium Nitrate.

XXI. Ammonium Nitrate		NH ₄ NO ₃			
✓	$\mu_{v, 25^\circ}$	$2 \mu_{v, 25^\circ}$	✓	$\mu_{v, 25^\circ}$	$2 \mu_{v, 25^\circ}$
1	93.87	187.7	50	124.0	248.0
2	101.0	202.0	100	126.8	253.6
4	107.0	214.0	200	129.9	259.8
5	108.2	216.4	400	131.7	262.4
10	114.5	229.0	500	131.8	263.6
20	119.6	239.2	1000	137.2	274.4
40	123.5	247.0	2000	137.8	275.6

In the comparison of the conductivities as the double salt has the composition $\text{Pr}(\text{NO}_3)_3 \cdot 2 \text{NH}_4\text{NO}_3$, we take the conductivity of the ammonium nitrate at one-half the dilution.

XXII. Comparisor.		Ammonium Praseodymium Nitrate.				
✓	$2 \mu_{v, 25^\circ}$ NH ₄ NO ₃	✓	$\mu_{v, 25^\circ}$ Pr(NO ₃) ₃	Sum.	$\mu_{v, 25^\circ}$ Double Salt	Difference.
1	187.7	2	146.0	333.7	265.6	68.1
2	202.0	4	170.9	372.9	344.3	28.6
4	214.0	8	200.8	414.8	400.2	14.6
5	216.4	10	213.9	430.3	413.9	16.4
10	229.0	20	236.8	465.8	459.2	6.6
20	239.2	40	258.3	497.5	496.5	1.0
40	247.0	80	280.9	527.9	528.3	-0.9
50	248.0	100	288.6	536.6	536.3	+ 0.3

100	253.6	200	308.4	562.0	560.8	+ 1.2
200	259.8	400	325.2	585.0	585.0	0.0
400	262.4	800	341.8	604.2	604.0	+ 0.2
500	263.6	1000	345.9	609.5	608.8	+ 0.7
1000	274.4	2000	359.3	633.7	631.0	+ 1.3
2000	275.6	4000	370.6	646.2	644.3	+ 1.9

DOUBLE NITRATE OF NEODYMIUM AND AMMONIUM.

The neodymium compounds at my disposal were the oxide, Nd_2O_3 , and the nitrate, $\text{Nd}(\text{NO}_3)_3$. As the amount of substance available was not large enough, on account of the tremendous solubility of neodymium salts, to prepare a perfectly, dry double nitrate of neodymium and ammonium by crystallizing from a solution containing the constituents and separating from the mother liquor, I made solutions of the constituent nitrates, standardized them, and mixed in equivalent proportions to make the salt $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3$.

As will be shown later such a mixture of salts is not necessarily exactly the same as a solution of the double salt itself, but its manner of ionization is not materially different, and at great dilutions, when the most interesting phenomena in connection with this investigation are found, the state of equilibrium is the same in the two cases.

I am well aware that this manner of preparing the double salt is open to many objections to its accuracy. The least excess of one constituent over the other will, of course, enter in very materially toward altering the conductivity. And since the equivalency of the quantities of the two solutions mixed is dependent upon the accuracy of both standardizations, the chance for error is comparatively large. I was not surprised, therefore, to find in the comparison of the dilute solutions, as will be seen in the tables given below, that the "difference" did not equal zero.

The neodymium nitrate was analysed in the same general way as the praseodymium nitrate. On the addition of ammonium hydroxide a light pink precipitate of the hydroxide comes down. Since neodymium does not form any higher oxide than Nd_2O_3 on ignition in air, the precipitate was not ignited in a stream of hydrogen.

Analysis of neodymium nitrate:-

I. 2 c.c. of solution gave 0.2836 gr. Nd_2O_3 .

II. 2 c.c. of solution gave 0.2826 gr. Nd_2O_3 .

The solution was therefore $\text{Nx}0.8445$, and its volume was 1.1840. It contained 278.45 grms. to the litre.

The ammonium nitrate solution was made up by weight and contained one gramme - molecule to the litre.

To prepare the solution of the salt $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3$ I mixed 98.66 c.c. of the neodymium nitrate solution with 166.66 c.c. of the ammonium nitrate solution, and diluted to five hundred c.c., making a solution of volume 6.

Conductivity of the double nitrate of neodymium and ammonium:-

XXIII. Ammonium Neodymium Nitrate. $\text{Nd}(\text{NO}_3)_3$. Molec.Wt. 489.96

V	Concentration.	Grms. per Litre.	$\mu_{\text{v}} 25^\circ$	
6	0.1666	81.66	520.2	
10	0.1000	48.996	570.9	
20	0.0500	24.498	624.7	
40	0.0250	12.249	674.0	
80	0.0125	6.129	713.6	
100	0.0100	4.8996	733.3	
200	0.0050	2.4498	770.2	
400	0.0025	1.2249	801.3	
800	0.00125	0.6129	833.9	
1000	0.00100	0.4899	850.2	
2000	0.00050	0.2449	877.0	
4000	0.00025	0.1224	884.8	

NEODYMIUM NITRATE.

The standardization of this solution has been given above
Conductivity of neodymium nitrate.

XXIV.

Neodymium Nitrate. $\text{Nd}(\text{NO}_3)_3$

Molec. wt. 329.72

v	Concentration	Grms. per Litre	μ_v 25°	
1.1840	0.8445	278.45	191.4	
2.368	0.4222	139.22	282.0	
4.736	0.2111	69.61	344.9	
9.472	0.1055	34.80	393.0	
23.68	0.0422	13.922	442.0	
47.36	0.0211	6.961	475.6	
94.72	0.0105	3.480	507.0	
236.8	0.0042	1.3922	539.6	
473.6	0.0021	0.6961	566.9	
947.2	0.0010	0.3480	578.6	
2368.0	0.0004	0.1392	599.9	
4736.0	0.0002	0.0696	611.4	

The conductivity of neodymium nitrate reduced to even volumes:-

(no. 1000 . .)

XXV. Neodymium Nitrate. $\text{Nd} (\text{NO}_3)_3$.

v	$\mu_{v \ 25^\circ}$	v	$\mu_{v \ 25^\circ}$	v	$\mu_{v \ 25^\circ}$
1	187.2	20	429.4	400	558.8
2	253.5	40	466.0	800	575.1
4	325.4	80	497.3	1000	579.8
8	373.1	100	510.5	2000	594.5
10	394.8	200	531.2	4000	600.4

The conductivity of ammonium nitrate has been given above.

XXVI. Comparison Ammonium neodymium nitrate.

v	$\frac{2\mu}{\text{NH}_4\text{NO}_3} \ 25^\circ$	v	$\mu_{v \ 25^\circ} \text{Nd} (\text{NO}_3)_3$	Sum	$\mu_{v \ 25^\circ} \text{Double Salt}$	Difference
5	216.4	10	394.8	611.2	570.9	40.3
10	229.0	20	429.4	658.4	624.7	33.7
20	239.2	40	446.0	705.2	674.0	31.7
40	247.0	80	497.3	744.3	713.6	30.7
50	248.0	100	510.5	758.5	733.3	25.2

100	258.6	200	581.2	7848	770.2	14.6
200	259.8	400	558.8	818.6	801.3	17.3
400	262.4	800	575.1	887.5	838.9	3.8
500	263.6	1000	579.3	843.4	850.2	- 6.8
1000	274.4	2000	594.5	868.9	877.0	- 6.1
2000	275.6	4000	600.4	876.0	884.8	- 8.8

It seems remarkable that the nitrates of two elements as closely related to each other as praseodymium and neodymium, should possess as different electrical conductivities. That of Neodymium nitrate is nearly 30 % larger than that of praseodymium nitrate. These salts are both exceedingly soluble in water and hygroscopic. Attention is called here, and will be again, in a later portion of this dissertation, to the fact that, although the determination of the molecular lowering of water by these substances does not increase regularly with increasing dilution but shows a reentrant bend in the curve, nevertheless the molecular conductivity increases regularly. The results show that ammonium praseodymium nitrate dissociates into its constituent molecules completely at about one-twentieth normal concentration and thereafter contracts itself as would a mixture of the constituent salts. The point of complete decomposition in the case of ammonium neodymium nitrate is at a volume of about 500.

Making use again of the data of Cronstchaff and Peckhoff¹¹⁾ for the conductivity of mixture of electrolytes, which do not form double salts, we find it recorded that the difference between ^{observed} ~~abroad~~ conductivity of the mixture and that calculated

¹¹⁾ Cronstchaff and Peckhoff, loc. cit.

from the constituents amounts, in the case of the solution $1/2$ ($KNO_3 + 1/2 Sr(NO_3)_2$), to less than one per cent. The difference found in the results recorded here for ammonium praseodymium nitrate is 20 % for a volume 1, and for ammonium neodymium nitrate 10 % of the sum of the conductivities of the constituents.

There is then no doubt of the existence of these nitrates at least partially unecomposed, in concentrated solution. They soon dissociate into their constituents, however, and conduct themselves like mixtures of the simple salts.

(1) Cronstedt and Beckhoff, loc. cit.

DOUBLE SULPHATES

Double Sulphate of Ammonium and Magnesium.

The double salt was prepared as usual by crystallizing out from a solution containing the constituent salts in equivalent proportions. The crystals were dried on absorbent paper and analysed.

In the analysis of both the crystals and the solution of the double salt, the magnesium was determined by precipitation with sodium phosphate.

Analysis of crystallized double salt.

1.1676 gr. gave 0.3615 gr. $Mg_2P_2O_7$

found 6.771 % Mg.

Theoretical % Mg. on basis of $MgSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
6.752

Analysis of solution of double salt -

- I. 5 cc solution gave 0.3458 gr. $Mg_2P_2O_7$
- II. 5 cc solution gave 0.3465 gr. $Mg_2P_2O_7$

The strength of the solution was therefore $N \times 0.6215$, and its volume 1.6090. It contained 224.21 gr. of the crystallized salt $MgSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$.

Conductivity of the Double Sulphate of Ammonium
and Magnesium.

XXVII. Ammonium Magnesium Sulphate Molec. wt. 360.76

v	Concentration	Gm per L. sol.	κ at 25°
1.609	0.6215	224.21	145.0
3.218	0.3107	112.10	187.7
6.436	0.1553	56.05	225.4
16.09	0.06215	22.42	265.5
32.18	0.03107	11.21	293.5
64.36	0.01553	5.605	333.4
160.9	0.006215	2.242	380.0
321.80	0.003107	1.121	409.4
643.60	0.001553	0.5605	443.9
1609.0	0.000621	0.2242	466.6
3218.0	0.000310	0.1121	494.3
6436.0	0.000155	0.0560	509.7

The conductivity of the double sulphates of ammonium
and magnesium calculated for equal volumes.

XXVIII.



ν	$M_{\nu 250}$	ν	$M_{\nu 250}$	ν	$M_{\nu 250}$
1	128.9	20	273.5	400	417.8
2	155.4	40	306.9	800	447.5
4	196.9	80	340.9	2000	473.3
8	231.9	200	387.1		

The conductivity of magnesium sulphate has been determined by a number of experimenters; by Kohlrausch (1) and Kranhals (2) at 18°, and Walden (3) at 25°. I have employed values which are made up from all three tables and are, I think, quite accurate. The three values did not differ very materially from one another.

XXIX.

Magnesium Sulphate Mg SO_4 Molec.wt. 120.42

ν	$M_{\nu 250}$	ν	$M_{\nu 250}$
2	62.6	80	139.3
4	76.7	200	165.9
8	89.1	400	184.3
20	110.0	800	199.5
40	123.4	2000	217.5

(1) Kohlrausch, Wied. Ann. 26, 161, (1885)

(2) Kranhals, Zeitschr. f. phys. Ch. 5, 250 (1890)

(3) Walden, Zeitschr. f. phys. Ch. 18, 1122, (1892)

Ammonium Sulphate.

The material employed was carefully purified by numerous crystallizations.

Analysis of solution.

- I. 10 c.c. solution
10 gave 0.2668 gr. Ba SO₄
- II. 10 c.c. solution
10 gave 0.2668 gr. Ba SO₄

The strength of the solution was, therefore, N X 1.1426 and its volume 0.8751.

Conductivity of ammonium sulphate.

XXX. Ammonium Sulphate. (NH₄)₂SO₄ Molec.wt. 132.22

V	Concentration	Grms. per Litre.	<i>M</i> 25°	
0.8751	1.1426	151.07	124.7	
1.75	0.5713	75.53	143.6	
3.50	0.2856	37.76	161.2	
8.751	0.11426	15.107	182.2	
17.50	0.05713	7.553	198.5	
35.	0.02856	3.776	215.0	
87.51	0.011426	1.5107	235.3	
175.	0.005713	0.7553	248.3	
350.	0.002856	0.3776	260.9	
875.1	0.001142	0.1510	269.5	
1750.	0.000571	0.0755	275.1	



Conductivity of ammonium sulphate calculated for even volumes.

XXXI.

Ammonium Sulphate.

v	$M_{v25^{\circ}}$	v	$M_{v25^{\circ}}$		$M_{v25^{\circ}}$
1	127.4	20	199.9	400	261.7
2	146.1	40	216.9	800	268.3
4	163.2	80	232.4	2000	276.6
8	179.2	200	250.1		

Comparison of conductivity of ammonium magnesium sulphate with the sum of the conductivities of its constituents.

XXXII.

Comparison Ammonium Magnesium Sulphate.

v	$M_{v25^{\circ}}$ Mg SO ₄	$M_{v25^{\circ}}$ (NH ₄) ₂ SO ₄	Sum	$M_{v25^{\circ}}$ Double Salt	Difference
2	62.6	146.1	208.7	155.4	53.3
4	76.7	163.2	239.9	196.9	43.0
8	89.1	179.2	268.3	231.9	36.4
20	110.0	199.9	309.9	273.5	36.4
40	123.4	216.9	340.3	306.9	33.4
80	139.3	232.4	371.7	340.9	30.8
200	165.9	250.1	416.0	387.1	28.9
400	184.3	261.7	456.0	417.8	28.2
800	199.5	268.3	467.8	447.5	20.3
2000	217.5	276.6	494.1	473.3	20.8

Double Sulphate of Ammonium and Copper.

The double salt was prepared in the usual way, and crystallizes easily from the solution with six molecules of water of crystallization. The crystallized salt was dried on absorbent paper and analysed.

Analysis of $\text{CuSO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.

The copper was precipitated with alkali and weighed as oxide. The sulphuric acid was determined as barium sulphate.

1.5630 gr. crystallized salt gave 0.3097 gr. Cu O

Found 19.81% Cu.

Theoretical 19.90% Cu.

0.1565 gr. gave 0.1818 gr. BaSO_4

Found 47.78% SO_4

Theoretical 48.04% SO_4

Analysis of solution of double sulphate of copper and ammonium:--

I. 10 c.c. solution gave 0.2575 gr. BaSO_4
10

II. 10 c.c. solution gave 0.2579 gr. BaSO_4
10

The solution was therefore N X 0.5516, and its volume 1.8128.

226.60 c.c. of this solution were then diluted to 250 c.c. to bring it to volume 2, and the dilutions were made from this as a mother-solution.

Conductivity of the double sulphate of copper and ammonium.

XXXIII. Ammonium Copper Sulphate. $(\text{NH}_4)_2\text{SO}_4\text{CuSO}_4$ Molec.wt. 400.0
cryst.400.0

	Concentration	Grms. per litre Cryst. salt.	25°	
2	0.50	200.00	161.6	
4	0.25	100.00	196.6	
8	0.125	50.00	226.0	
20	0.050	20.00	267.3	
40	0.025	10.00	296.8	
80	0.0125	5.00	331.0	
200	0.0050	2.00	377.3	
400	0.0025	1.00	406.9	
800	0.00125	0.50	434.1	
2000	0.00050	0.20	470.0	

Copper Sulphate.

(1)

Kohlrausch has determined the conductivity of copper sulphate at 18°. I have employed his results changing them to their value at 25° by the use of the factor 2.25, and have interpolated wherever necessary.

XXXIV. Copper Sulphate, CuSO_4 . Molec.wt. 159.66

v	M. 25°		M. 25°	v	M. 25°
1	43.4	20	98.1	400	1742
2	55.8	40	109.8	800	1923
4	66.6	80	128.4	2000	219.8
8	74.5	200	156.2		

(1) Kohlrausch. Wied. Ann. 26. 161. 1885.

The conductivity of ammonium sulphate has been given above.

Comparison of the conductivity of ammonium copper sulphate with the sum of the conductivities of its single constituents.

XXXV. Comparison Ammonium Copper Sulphate.

✓	$\frac{1}{N} \cdot 250$ (NH ₄) ₂ SO ₄	$\frac{1}{N} \cdot 250$ CaSO ₄	Sum	$\frac{1}{N} \cdot 250$ Double salt.	Difference
1	127.4	43.4	170.8		
2	146.1	55.8	201.9	161.6	40.3
4	163.2	66.6	229.8	194.6	35.2
8	179.2	74.5	253.7	220.0	33.7
20	199.9	98.1	298.0	266.8	32.2
40	216.9	109.8	326.7	296.8	29.9
80	232.4	128.4	360.8	330.8	30.0
200	250.1	156.2	406.3	377.3	29.0
400	261.7	174.2	435.9	406.9	29.0
800	268.3	192.3	460.6	434.1	26.5
2000	276.6	219.8	496.4	470.0	26.4

Ferrous Ammonium Sulphate.

The substance used was the so-called "chemically pure" ammonio-ferrous sulphate of Theodor Schuchart. It was found that the solution decomposed so quickly at 25° that the conductivity of only four dilutions was measured.

The solution was made up by weighing out the substance so as to have a concentration $N \times 0.5$. It was also standardized by precipitation with barium chloride.

- I. 10 c.c. $\frac{\text{solution}}{10}$ gave 0.2331 gr. BaSO_4
 II. 10 c.c. $\frac{\text{solution}}{10}$ gave 0.2331 gr. BaSO_4

The solution, therefore, has a volume 2.0003.

Conductivity of ammonio-ferrous sulphate.

XXXVI. Ammonio-Ferrous Sulphate. $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$.
 Molec.wt.cryst. 392.40

	Concentration	Grms.cryst.salt per Litre.	25°	
2	0.5	196.20	156.6	
20	0.05	19.62	261.9	
200	0.005	1.962	361.8	
2000	0.0005	0.1962	466.5	

The solution oxidized in the course of the measurements so that they are not given as accurate.

Ferrous Sulphate.

The ferrous sulphate used was made by dissolving an excess of iron (piano wire) in sulphuric acid. The concentration was carried on also with excess of metal present.

The substance was analysed by precipitation of the sulphuric acid.

- I. 10 c.c. of $\frac{\text{solution}}{10}$ gave 0.1089 gr. BaSO_4
 II. 10 c.c. of $\frac{\text{solution}}{10}$ gave 0.1087 gr. BaSO_4

The solution was, therefore, N X 0.4664 and its volume 2.1440. It contained 70.92 grms. of the anhydrous salt to the litre.

Conductivity of ferrous sulphate.

XXXVII. Ferrous Sulphate. FeSO_4 . Molec. wt. 152.06

\checkmark	Concentration	Grms. per litre.	\checkmark 25°	
2.144	0.4664	70.92	59.8	
21.44	0.0466	7.092	104.5	
214.4	0.0046	0.7092	171.0	
2144	0.0004	0.07092	233.0	

The same calculated for even volumes.

XXXVIII. Ferrous Sulphate.

\checkmark	\checkmark 25°	\checkmark	\checkmark 25°	
2	59.4	200	170.6	
20	104	2000	232.0	

The conductivity of ammonium sulphate has been given above.

Comparison of the conductivity of ammonio-ferrous sulphate with the sum of the conductivities of its constituents.

XXXIX. Comparison Ammonio-Ferrous Sulphate.

κ	κ_{25° (NH_4) $_2\text{SO}_4$	κ_{25° FeSO_4	Sum	κ_{25° Double Salt.	Difference.
2	146.1	59.4	205.5	156.6	48.9
20	199.9	104.0	303.9	261.9	42.0
200	250.1	170.6	420.7	361.8	58.9
2000	276.6	232.0	508.6	466.5	42.1



DOUBLE SULPHATE OF AMMONIUM AND CADMIUM.

The salt was prepared as usual by crystallizing from a solution of its constituents.

The crystallized salt $(\text{N H}_4)_2 \text{SO}_4 \cdot \text{Cd SO}_4 \cdot 6\text{H}_2\text{O}$ was dried on absorbent paper and analyzed. The cadmium was precipitated as carbonate and weighed as oxide in a Gooch crucible. The sulphuric acid was determined in the usual way.

Analysis of crystallized salt.

I. 1.3243 gr. gave 0.3742 gr. CdO

and 1.3785 gr. Ba SO_4 .

II. 1.2640 gr. gave 0.3526 gr. CdO and

1.3140 gr Ba SO_4 .

	I	II
Cadmium found	24.71 %	24.40 %

Theoretical Cadmium in $(\text{NH}_4)_2 \text{SO}_4 \cdot \text{Cd SO}_4 \cdot 6 \text{H}_2\text{O}$. . . 24.97%

SO_4 found 42.80 % ; 42.76 %

Theoretical SO_4 in $(\text{NH}_4)_2 \text{SO}_4 \cdot \text{Cd SO}_4 \cdot 6\text{H}_2\text{O}$. . . 42.80 %

Analysis of Solution.

I. 2 cc gave 0.9229 gr. Ba SO_4

II. 2 cc gave 0.9240 gr. Ba SO_4 .

The solution was therefore N X 0.9383 and its volume

1.0113. I then diluted 101.13 cc to 200 to bring to a volume 2, and used this as a mother-solution in subsequent dilutions.

Conductivity of the double sulphate of ammonium and cadmium.

X L Ammonium Cadmium Sulphate, $\text{Cd SO}_4 (\text{N H}_4)_2 \text{SO}_4$ Molec. Wt.
cryst. 443.40

✓	Concentration	Grams. per Litre	
2	0.50	224.20	151.6
4	0.25	112.10	1185.0
8	0.125	56.05	216.0
20	0.050	22.42	254 .4
40	0.025	11 .21	285.5
80	0.0125	5.605	320.6
200	0.0050	2.242	366.2
400	0.0025	1.121	398.4
800	0.00125	0.5605	432.2
2000	0.00050	0.2242	474.0



Cadmium Sulphate.

Analysis of solution of Cadmium sulphate.

I. 4 c.c. solution gave 0.6823 gr. Cd O.

II. 4 c. c. solution gave 0.6838 gr. CdO.

The solution was therefore N X 1.3343 and its volume 0.7496.

It contained 277.61 gr. Cadmium sulphate to the litre.

Conductivity of Cadmium Sulphate.

XLI Cadmium Sulphate Cd SO_4 Molec. Wt. 208.06

	Concentration	Gms. per litre	
0.75	1.3343	277.61	32.5
1.50	0.6671	138.30	45.5
3.00	0.3335	69.40	57.1
7.50	0.1334	27.76	71.8
15.00	0.0667	13.83	84.4
30.00	0.0333	6.94	99.6
75.00	0.0133	2.77	115.2
150.00	0.0066	1.39	130.0
300.00	0.0033	0.69	165.2
750.00	0.0013	0.27	190.5
1500.00	0.0006	0.14	209.2
3000.00	0.0003	0.07	225.7

THE HISTORY OF THE

REIGN OF KING CHARLES THE FIRST

BY JOHN BURNET

IN TWO VOLUMES

LONDON

Printed by J. Sturges, at the Angel in St. Dunstons Church

in the Strand

1724

Printed by J. Sturges, at the Angel in St. Dunstons Church

in the Strand

1625	1626	1627	1628
1629	1630	1631	1632
1633	1634	1635	1636
1637	1638	1639	1640
1641	1642	1643	1644
1645	1646	1647	1648
1649	1650	1651	1652
1653	1654	1655	1656
1657	1658	1659	1660
1661	1662	1663	1664
1665	1666	1667	1668
1669	1670	1671	1672
1673	1674	1675	1676
1677	1678	1679	1680
1681	1682	1683	1684
1685	1686	1687	1688
1689	1690	1691	1692
1693	1694	1695	1696
1697	1698	1699	1700

The same calculated for intermediate volumes.

XLII

Cd SO ₄					
v	$\mu_{v, 25^\circ}$	v	$\mu_{v, 25^\circ}$	v	$\mu_{v, 25^\circ}$
1	36.8	20	89.6	400	170.8
2	49.4	40	103.1	800	191.7
4	60.4	80	122.5	2000	214.7
8	72.6	200	150.7		

The conductivity of ammonium sulphate has been given above.

Comparison of the conductivity of the double sulphate of ammonium and cadmium with the sum of the conductivities of its constituents.

XLIII Comparison. Ammonium Cadmium Sulphate.

v	$(\text{NH}_4)_2\text{SO}_4$ $\mu_{v, 25^\circ}$	CdSO_4 $\mu_{v, 25^\circ}$	Sum	Double Salt $\mu_{v, 25^\circ}$	Difference.
2	146.1	49.4	195.5	151.6	43.9
4	163.2	60.4	223.6	185.0	38.6
8	179.2	72.6	251.8	216.0	35.8
20	199.2	89.6	289.5	254.4	35.1
40	216.9	103.1	320.0	285.5	34.5
80	232.4	122.5	354.9	320.6	34.3
200	250.1	150.7	400.8	366.2	34.6
400	261.7	170.8	432.5	398.4	34.1
800	268.3	191.7	460.0	432.2	27.8
2000	276.6	214.7	491.3	474.0	27.0

DOUBLE SULPHATE OF AMMONIUM AND NICKEL.

The salt employed was manufactured by Dr. Theodor Schuchart.

Analysis of crystallized $\text{Ni SO}_4 \cdot (\text{N H}_4)_2 \text{SO}_4 \cdot 6\text{H}_2 \text{O}$.

I. 0.5642 gave 0.6665 gr Ba SO_4

II. 0.4823 gave 0.5695 gr. Ba SO_4 .

Found I II
 48.53 % 43.57 % SO_4

Theoretical % SO_4 in $\text{Ni SO}_4 \cdot \text{K}_2 \text{SO}_4 \cdot 6\text{H}_2 \text{O}$ 43.63

Analysis of solution.

I 10 cc solution gave 0.6222 gr. Ba SO_4

II 10 cc solution gave 0.6244 gr. Ba SO_4 .

The concentration of the solution was therefore 0.1337, and its volume 7.4795. 467.47 cc were diluted to 500 cc to bring to a volume 8 and this was employed as the mother solution for subsequent dilutions.

Conductivity of the double sulphate of nickel and ammonium :-

XLIV Ammonium Nickel Sulphate $\text{Ni SO}_4 \cdot (\text{N H}_4)_2 \text{SO}_4$.
Molec. Wt. cryst. 395.10

✓	Concentration	Gr. per Litre	
8	0.125	49.89	224.1
20	0.050	19.755	263.4
40	0.025	9.377	293.8
80	0.0125	4.933	322.3
200	0.0050	1.9755	370.1
400	0.0025	0.9377	404.8
800	0.00125	0.4933	439.4
2000	0.00050	0.19755	484.6

THE HISTORY OF THE UNITED STATES

OF AMERICA

FROM THE FIRST DISCOVERY OF THE CONTINENT

TO THE PRESENT TIME

BY

JOHN F. JOHNSON

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AND

NICKEL SULPHATE.

Analysis of solution :-

I. 10 cc solution gave 0.5341 gr. Ba S₆⁴.

II. 10 cc solution gave 0.5359 gr. Ba SO₄.

The solution had therefore a concentration of NXO.2295 and a volume 4.3570.

272.31 c c were diluted to 500 cc to bring to a volume of 8 and this was used as the mother-solution in subsequent dilution.

Conductivity of Nickel Sulphate.

XLV NICKEL SULPHATE NiS O₄. Molec. wt. 154.76

✓	Concentration	Grms. per litre	$\mu_{v, 25^\circ}$
8	0.125	19.34	77.9
20	0.050	7.738	96.1
40	0.025	3.869	109.0
80	0.0125	1.934	122.8
200	0.0050	0.7738	152.0
400	0.0025	0.3869	173.1
800	0.00125	0.1934	194.8
2000	0.00050	0.07738	232.3

The conductivity of ammonium sulphate has been given above.

Comparison of the conductivity of the double sulphate of nickel and ammonium with the sum of the conductivities of its constituents.

XLVI COMPARISON. . NICKEL AMMONIUM SULPHATE.

V	$(\text{NH}_4)_2\text{SO}_4$ At 25°	NiSO_4 At 25°	Sum	Double Salt At 25°	Difference
8	179.2	77.9	257.1	224.1	33.0
20	199.9	96.1	296.0	263.4	32.6
40	216.9	109.0	325.9	293.8	32.1
80	232.4	122.8	355.2	322.5	32.9
200	250.1	152.0	402.1	370.1	32.0
400	261.7	173.1	434.8	404.6	30.2
800	268.3	194.3	463.1	439.4	23.7
2000	276.6	232.3	508.9	484.6	24.3

DOUBLE SULPHATE OF POTASSIUM AND NICKEL.

The salt was made in the usual way by crystallization from a solution containing its constituents in equivalent proportions.

Analysis of crystallized $\text{K}_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$.

1.3474 gr. salt gave 1.4352 gr. BaSO_4 .

Found, 43.82 % SO_4 .

Theoretical, 43.93 % SO_4 .

Analysis of solution of double salt,-

I 5 cc solution gave 0.4005 gr. BaSO_4 .

II. 5 cc solution gave 0.4002 gr. BaSO_4 .

The solution was therefore N X 0.1713, and its volume 5.336. 364.75 cc were then diluted to 500 cc to bring to volume 8 and this was employed as the mother-solution in subsequent dilution.

Conductivity of potassium Nickel Sulphate,-

XLVII.

Potassium Nickel Sulphate,

$\text{NiSO}_4, \text{K}_2 \text{SO}_4$. Molec. Wt. cryst. 435.24

	Concentration	Grms per Litre. Cryst. Salt.	
8	0.125	54.40	219.5
20	0.050	21.762	261.5
40	0.025	10.331	291.6
80	0.0125	5.440	323.7
200	0.0050	2.1762	369.4
400	0.0025	1.0831	400.2
800	0.00125	0.5440	438.0
2000	0.00050	0.21762	494.3

The conductivity of Nickel sulphate has been given above.

The conductivity of potassium sulphate has been determined by a number of observers. I take the values of Mackay⁽¹⁾ obtained for 25°.

(1) Mackay. J. H. U. Diss. 1896 ; An. Ch. Jr. 19, 83.

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XLVIII Potassium Sulphate, K_2SO_4 . Molec. Wt. 174.36

v	Concentration.	Gr. per Litre.	M_v	
8	0.125	21.795	182.4	
20	0.050	3.718	205.1	
40	0.025	4.359	220.3	
80	0.0125	2.1795	237.9	
200	0.0050	0.8718	252.4	
400	0.0025	0.4359	262.2	
800	0.00125	0.21795	273.0	
2000	0.00050	0.08718	276.5	

Comparison of conductivity of double sulphate of nickel and potassium with the sum of the conductivities of its constituents.

XLIX Comparison. Potassium Nickel Sulphate.

v	K_2SO_4 $M_{v,25^\circ}$	$NiSO_4$ $M_{v,25^\circ}$	Sum	$M_{v,25^\circ}$ Double salt.	Difference
8	182.4	77.9	260.3	219.5	40.8
20	205.1	96.1	301.2	261.5	39.7
40	220.3	109.0	329.3	291.6	37.7
80	237.9	122.8	360.7	323.7	37.0
200	252.4	152.0	404.4	369.4	35.0
400	262.2	173.1	435.3	400.2	35.1
800	273.0	194.8	467.8	438.0	29.0
2000	276.5	232.3	508.8	474.3	14.5

The results with double sulphates show they all remain undissociated to about the same extent. In a half normal solution the "difference" amounts in the case of ammonium magnesium sulphate to 25% ; in ammonium copper sulphate to 29 % ; in ammonium ferrous sulphate to 23 % ; in ammonium cadmium sulphate to 22 % of the sum of the individual conductivities of the constituents. In the cases of nickel ammonium and nickel potassium sulphates the difference at a volume 8 about equals that of the other sulphates at the same dilution ; more concentrated solutions were not measured since these salts are not sufficiently soluble.

Klein⁽¹⁾ showed that a mixture of sodium and potassium sulphates has a conductivity which is about 1 % less than that calculated from its constituents. The difference here is much larger. Jones and Mackay⁽²⁾ found a greater difference in the alums studied by them---from 2 1/2 to 11 per cent.

This would seem to indicate that the double sulphates which are not alums exist to a greater degree undissociated in aqueous solution than the alums. The difference was found to disappear at a dilution of about 400 litres in the case of the the alums while in the case of the sulphates under investigation it did not disappear at the dilution of 2000.

(1) Klein, loc. cit.

(2) Jones & Mackay, loc. cit.

Conductivity of Potassium acid Sulphite.

LI $KHSO_3$

v	$\frac{1}{v} \text{ at } 25^\circ$	$\frac{1}{v} \text{ at } 25^\circ$	
32	101.9	203.8	
64	106.5	213.0	
128	110.7	221.4	
256	114.7	229.4	
512	118.6	237.2	
1024	121.8	243.6	

IN making the comparison of conductivities heret that of the potassium acid sulphite must be taken at one half the dilution and doubled.

LII Comparison. Potassium Acid Sulphite.

v	$\frac{1}{v} \text{ at } 25^\circ$ $K_2SO_3 + H_2SO_3$	$\frac{1}{v} \text{ at } 25^\circ$ $KHSO_3$	Difference
32	336.1	203.8	182.3
64	433.9	213.0	225.9
128	484.7	221.4	263.3
256	525.0	229.4	295.6
512	557.9	237.2	320.7
1024	586.5	243.6	342.9

Potassium Bisulphate.

The data for this comparison of conductivities have been recorded. The conductivity of potassium sulphate has been



determined at 25° by Walden (1) . That of sulphuric acid by Douglas in this laboratory, and that of potassium acid sulphate by Barth. (2)

The conductivity of potassium sulphate and sulphuric acid are given below.

LIII. Potassium Sulphate and Sulphuric Acid.

v	K_2SO_4 At 25°	H_2SO_4 At 25°	Sum
64	232.2	511.0	743.2
128	246.0	581.3	827.3
256	256.3	612.0	868.3
512	265.4	673.5	938.9
1024	272.8	713.9	986.7
2048	278.6	715.9	994.5

(1) Walden, Zeitschr f. ph. Chem. 2, 49, 1888.

(2) BARTH. loc. cit.

The conductivity of the potassium bisulphate is given below.

LIV POTASSIUM ACID SULPHATE, $KHSO_4$

v	μ_{25°	κ_{25°	
32	318.5	837.0	
64	361.06	723.2	
128	401.8	803.6	
256	440.8	881.6	
512	476.0	952.0	
1024	498.0	996.0	

The comparison is made in the same manner as in the case of potassium bisulphite.

LV. Comparison. Acid Potassium Sulphate.

v	μ_{25° $K_2SO_4 + H_2SO_4$	κ_{25° $KHSO_4$	Difference.	
64	743.2	723.2	20.0	
128	827.3	803.6	23.7	
256	863.8	881.6	-12.8	
512	938.9	952.0	-13.1	
1024	986.7	996.0	-9.3	
2048	994.5			

The results with these acid^{sa} are difficult to interpret. It would seem that the existence of the acid sulphite is proved but the acid sulphate is much more easily broken down by the process of solution.

Direct Comparison of Double Salt and Mixture.

Through the work referred to in this paper the conclusion has been reached that double salts in concentrated solution dissociate to a greater or less extent as if they were salts of complex acids, and then, as the dilution increases, the complex ion dissociates into simpler ions.

The question now arises, is the state of equilibrium the same in a solution of a double salt as it is in a mixture of solution of the constituents having the same concentration as the double salt? It seemed desirable to test this question as thoroughly and carefully as possible.

At my request, therefore, Mr. C. F. Lindsay undertook the task to determine whether there is any difference between the conductivity of a double salt and the conductivity of a mixture of the constituents having the same concentration. This work is given here, together with a repetition of a portion of it by myself.

The method of work was the same as that described above. The solution of the double salt was carefully standardized and the conductivity determined. Then a solution of each

of the constituent salts was prepared and accurately standardized. From these analyses the volumes of the two solutions which would contain the salts in the same proportion in which they exist in the double salt, were calculated. These volumes of the two solutions were mixed in a measuring flask, and the whole diluted to a known volume. This mixture was then standardized gravimetrically to see that no error had been made in bringing the constituents together and in the dilution. This standardized solution, which in every case was found to contain the constituents to almost exactly the extent calculated, was used as the mother solution in subsequent dilutions.

The same cell was used to measure the conductivity of the double salt as was employed with the mixture and they were generally measured as nearly as possible at the same time in order that the temperature of the thermostat (which was regulated within 0.1° by an Ostwald regulator) might be the same. The same apparatus was used throughout in the manipulation of the double salt and the mixture.

LVI. Double Chloride of Potassium and Cadmium.
 $\text{KCl} \cdot \text{CdCl}_2$

	Double Salt $\text{KCl} \cdot \text{CdCl}_2$ <i>At 25°</i>	Mixture $\text{KCl} + \text{CdCl}_2$ <i>At 25°</i>	Difference
2	117.8	119.4	1.6
4	146.3	148.1	1.8
8	172.4	174.9	2.5
20	208.4	209.3	0.9

The conductivity of the double chloride is, then, less than the conductivity of the mixture of the two chlorides. The difference in this case and in all other cases tried, is always small, but is larger than all known experimental errors, and is always in the same direction, i.e. the mixture has the higher conductivity.

LVII. Double Sulphate of Potassium and Nickel. $K_2SO_4NiSO_4$

v	Double Salt $K_2SO_4NiSO_4$ <i>At 25°</i>	Mixture $K_2SO_4NiSO_4$ <i>At 25°</i>	Difference
6	213.68	216.31	2.63
12	244.38	246.61	2.23
24	273.31	276.02	2.71
60	314.13	314.35	0.22

LVIII. Double Sulphate of Ammonium and Magnesium $MgSO_4(NH_4)_2SO_4$

v	Double Salt $MgSO_4(NH_4)_2SO_4$ <i>At 25°</i>	Mixture $MgSO_4 + (NH_4)_2SO_4$ <i>At 25°</i>	Difference
2	159.7	164.6	4.9
4	197.7	202.4	4.7
8	231.5	237.1	5.5
20	273.9	277.9	4.0

Repeated, making and standardizing solutions anew.

LIX. Ammonium Magnesium Sulphate. $(\text{NH}_4)_2\text{SO}_4$ MgSO_4

v	Double Salt $\text{MgSO}_4(\text{NH}_4)_2\text{SO}_4$ <i>11.25</i>	Mixture $\text{MgSO}_4 + (\text{NH}_4)_2\text{SO}_4$ <i>11.25</i>	Difference
5.09	212.70	216.78	4.08
10.18	243.89	248.28	4.39
25.46	284.80	289.10	4.30

Repeated, making and standardizing solutions anew.

3.09	189.9	193.2	3.3
------	-------	-------	-----

Repeated, making and standardizing solutions anew.

6.064	216.03	219.96	3.93
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LX. Ammonium Cadmium Sulphate $(\text{NH}_4)_2\text{SO}_4$ CdSO_4

l	Double Salt $\text{CdSO}_4(\text{NH}_4)_2\text{SO}_4$ <i>11.25</i>	Mixture $\text{CdSO}_4 + (\text{NH}_4)_2\text{SO}_4$ <i>11.2</i>	Difference
3.036	171.94	173.25	1.31
3.001	171.7	172.4	0.7

From these results the conclusion is reached that the conductivity of a double salt in concentrated solutions is slightly less than the conductivity of a mixture of the constituents having the same concentration as the double salt.

It appears that the double salt when once formed does not dissociate in exactly the same way or to the same extent as the mixture of the constituents which have never united to form the double salt.

This conclusion is so different from what we should expect that it was decided to test it in another way. The conductivity of a solution of the mixed salts was determined and a measured volume of the mixture then placed in a platinum dish and evaporated to dryness. Under these conditions there would be formed, at least in part, the double salt. This residue was then dissolved in some of the same pure water in which the mixture of the two salts was originally dissolved, and diluted to exactly the same volume.

If the double salt has a smaller conductivity than the mixture of the constituents at the same dilution, the second solution, containing the residue from the evaporation, should have a smaller conductivity than the original solution of the mixture at the same concentration.

The experiment was tried with the double sulphate of potassium and nickel. A solution containing the two sulphates in equimolecular quantities was evaporated nearly to dryness and the residue dissolved and diluted to exactly the same volume.

LXI.

 $\text{NiSO}_4 \text{ K}_2\text{SO}_4$

v		
24	11, 21 of mixture before evaporation	276.02
24	" " " after "	274.59
24	" " double salt	273.31
12	" " mixture before evaporation	246.61
12	" " " after "	245.14
12	" " double salt	244.38

In both these experiments the mixture before evaporation had a larger conductivity than after evaporation. This agrees exactly with what was found above, since in the process of evaporation some of the double salt was formed. The mixture after evaporation had a larger conductivity than the solution of the double salt of the same concentration. This is also what is to be expected since, in the rapid evaporation, only a portion of the double salt was formed.



CRYSCOPIC WORK.LXII MERCURY POTASSIUM CYANIDE. $K_2 Hg (CN)_4$.

ν	Gr. per Litre	Concentration.	$\begin{matrix} L \\ \text{Lowering} \end{matrix}$	$\begin{matrix} \Delta \\ \text{Mol. Depres-} \\ \text{tion.} \end{matrix}$
2.442	153.74	0.4095	1.902°	4.64
4.384	73.37	0.2047	0.971°	4.74
12.210	27.35	0.0819	0.405°	4.94

LXIII MERCURIC CYANIDE $Hg (C N)_2$

ν	Gr. per Litre	Concentration	$\begin{matrix} L \\ \text{Lowering} \end{matrix}$	$\begin{matrix} \Delta \\ \text{Mol.} \\ \text{Depression} \end{matrix}$
5	50.473	0.2	0.337°	1.93

LXIV Potassium Cyanide, $K C N$.

ν	Gr. per Litre.	Concentration	$\begin{matrix} L \\ \text{Lowering} \end{matrix}$	$\begin{matrix} \Delta \\ \text{Mol. Dep.} \end{matrix}$
1.1034	59.08	0.9063	3.385°	3.73
1.4343	45.45	0.6372	22.623°	33.76
2.3686	22.72	0.3436	1.321°	3.79
7.4129	8.73	0.1349	0.531°	3.93

XLV Comparison, Potassium Mercury Cyanide.

v	2Δ KCN	v	Δ $Hg(CN)_2$	Sum	Δ Double Salt	Difference
2.5	7.57	5	1.93	9.50	4.73	4.77

LXVI CADMIUM POTASSIUM IODIDE, $K_2 Cd I_4$

v	Gr. per Litre	Concentration	Lowering \downarrow	Molec. Dep. Δ
2.302	303.08	0.4344	3.3730°	8.927
2.762	252.56	0.362	3.177°	8.776
5.524	126.28	0.181	1.557°	8.602
9.207	75.77	0.1036	0.960°	8.84
13.310	50.51	0.0724	0.664°	9.17

This salt shows a minimum point in the curve of molecular depressions between the volumes 2.7 and 5.5 or between the volumes 5.5 and 9.2. The comparison was therefore not attempted and the molecular depressions of the constituents were not ascertained.

This phenomenon has been noticed before. Jones and Mackay (1)

(1) Jones and Mackay, loc. cit.

and Jones and Ota (1) attempted to apply the cryoscopic method in the same way as it is here applied but without great success. A special study of those substances which had been found to give this minimum in concentrated solution was made by Jones and Chambers (2) and later extended by Chambers and Frazier (3). They accounted for the phenomenon by supposing the formation in concentrated solution of hydrated compounds. The substances under consideration at present then, together with others mentioned below, must now be added to those heretofore known to possess this property.

LXVII AMMONIUM CADMIUM SULPHATE $(\text{NH}_4)_2 \text{SO}_4 \cdot \text{Cd SO}_4$.

γ	Gr. per Litre.	Concentration	Δ Lowering	Mol. Dep.
1.6347	202.03	0.6117	3.052°	4.99
2.0433	161.64	0.4394	2.493°	5.09
2.7243	121.11	0.3670	1.914°	5.21
4.0866	80.82	0.2447	1.345°	5.49 5.88
8.1732	40.41	0.1223	0.719°	
16.3464	20.20	0.0612	0.378°	6.17

- (1) Jones and Ota, *loc cit.*
 (2) Jones and Chambers, *Am. Ch. Jr.* 23, 89, (1900).
 (3) Chambers and Frazier, *Am. Ch. Jr.* 23, June 1900.

LXVIII Cadmium Sulphate, CdSO_4

v	Gr. per Litre	Concentration	Lowering L	Mol. Dep. Δ
0.7502	277.30	1.3323	2.526°	1.87
1.0004	207.97	0.9996	1.774°	1.77
1.5004	138.64	0.6664	1.175°	1.73
1.876	110.89	0.533	0.933°	1.75
2.50	83.22	0.400	0.714°	1.78
3.752	55.13	0.2665	0.505°	1.89
7.504	27.56	0.1333	0.263°	1.93

This salt shows the reentrant bend in the curve of molecular depressions, the minimum point coming at about a volume of 1.5.

(+)

LXIX Ammonium Sulphate, $(\text{NH}_4)_2\text{SO}_4$

v	Gr. per Litre	Concentration	Lowering L	Mol. Dep. Δ
5	26.432	0.2	0.829	4.14
10	13.216	0.1	0.437	4.37

14.28	9.2512	0.07	0.316°	4.51
20.	6.608	0.05	0.237°	4.74
33.33	3.9648	0.03	0.148°	4.93
66.66	1.9824	0.015	0.075°	5.00

LXX Comparison. Ammonium Cadmium Sulphate.

v	Δ Cd S O ₄	Δ (₂) ₂ SO ₄	Sum	Δ Double Salt	Dif.
5	1.90	4.14	6.04	5.57	0.47

LXXI

Copper Ammonium Sulphate. $\text{CuSO}_4 (\text{NH}_4)_2 \text{SO}_4$

v	Gr. per Litre	Concentration	Lowering Δ	Mol. Dep. Δ
3.069	130.32	0.3258	1.736°	5.32
6.138	65.16	0.1629	0.990°	6.07

1	100	100	100
2	100	100	100
3	100	100	100
4	100	100	100

5	100	100	100
6	100	100	100
7	100	100	100
8	100	100	100

9	100	100	100
10	100	100	100
11	100	100	100
12	100	100	100

13	100	100	100
14	100	100	100
15	100	100	100
16	100	100	100

17	100	100	100
18	100	100	100
19	100	100	100
20	100	100	100

21	100	100	100
22	100	100	100
23	100	100	100
24	100	100	100

25	100	100	100
26	100	100	100
27	100	100	100
28	100	100	100

29	100	100	100
30	100	100	100
31	100	100	100
32	100	100	100

33	100	100	100
34	100	100	100
35	100	100	100
36	100	100	100

LXXII

Praseodymium Nitrate $\text{Pr}(\text{NO}_3)_3$

ν	Gr. per Litre	Concentration	Lowering L	Mol. Dep. Δ
2.6305	124.15	0.38015	2.184	5.74
5.2610	62.07	0.19007	1.054 °	5.53
10.5220	31.03	0.09503	0.543 "	5.71
21.0440	15.51	0.04752	0.284 °	5.97

This salt does not give a regular rise in the molecular depression with increasing dilution, but decreases, reaching a minimum between the volumes 2 and 10. It therefore falls into the same category with those salts described by Jones and Chambers ⁽¹⁾.

The same calculated for even volumes.

LXXIII

Praseodymium Nitrate.

v	Concentration	Molec. Lowering Δ	
2	0.5	5.79	
4	0.25	5.63	
8	0.125	5.63	
20	0.050	5.95	

LXXIV

AMMONIUM NITRATE, NH_4NO_3

✓	Concentration	Gr. per Litre	Lowering L	Δ Mol. Dep.	2 Molec. Dep. 2 Δ
1	1.0	80.12	3.136°	3.13	6.27
2	0.5	40.06	1.629°	3.26	6.52
4	0.25	20.03	0.863°	3.45	6.90
10	0.10	8.012	0.363°	3.63	7.26

(1) Jones and Chambers, Am. Ch. Jr. 23, 89.

LXXV

Praseodymium Ammonium Nitrate. $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{NH}_4\text{NO}_3$

v	Concentration	Gr. per Litre	Lowering L	Molec. Dep. A
0.8314	1.2027	563.40	16.50	13.71
1.6628	0.6013	284.20	7.50	12.47
3.3256	0.3006	142.10	3.6370	12.09
8.314	0.12027	56.84	1.7790	14.79
16.628	0.06013	28.42	0.8870	14.79

This double salt exhibits the phenomenon of the minimum in the molecular depression. As this is not observed in the case of ammonium nitrate we must ascribe it to the influence of the praseodymium nitrate.

The same calculated for even volumes.

LXXVI.

Praseodymium Ammonium Nitrate.

v	Concentration	Molec. Dep. L
2	0.5	12.40
4	0.25	12.45
8	0.125	14.63
20	0.050	

LXXVII

Comparison. Praseodymium Ammonium Nitrate.

v	2Δ NH_4NO_3	v	Δ $\text{Pr}(\text{NO}_3)_3$	Sum	Δ Double Salt	Difference
1	6.27	2	5.79	12.06	12.40	-0.36
2	6.52	4	5.63	12.15	12.45	-0.30
4	6.90	8	5.63	12.53	14.63	-2.10
10	7.26	20	5.95	13.21		



LXXVIII Neodymium Ammonium Nitrate. $\text{Nd}(\text{NO}_3)_3 \cdot 2\text{NH}_4(\text{NO}_3)$.

✓	Concentration	Gr. per Litre	Lowering L	Molec. Dep. Δ	
6	0.1666	81.66	3.007°	18.10	
10	0.1	48.99	1.836°	18.36	
20	0.05	24.49	0.927°	18.54	T

LXXIX

Neodymium Nitrate $\text{Nd}(\text{NO}_3)_3$

v	Concentration	Gr. per Litre	Lowering L	Molec. Dep.
1.1840	0.8446	278.45	10.05°	11.89
2.3680	0.4223	139.22	4.969°	11.76
4.736	0.2111	69.61	2.456°	11.63
9.472	0.1055	34.80	1.254°	11.88
23.68	0.04223	13.92	0.522°	12.36

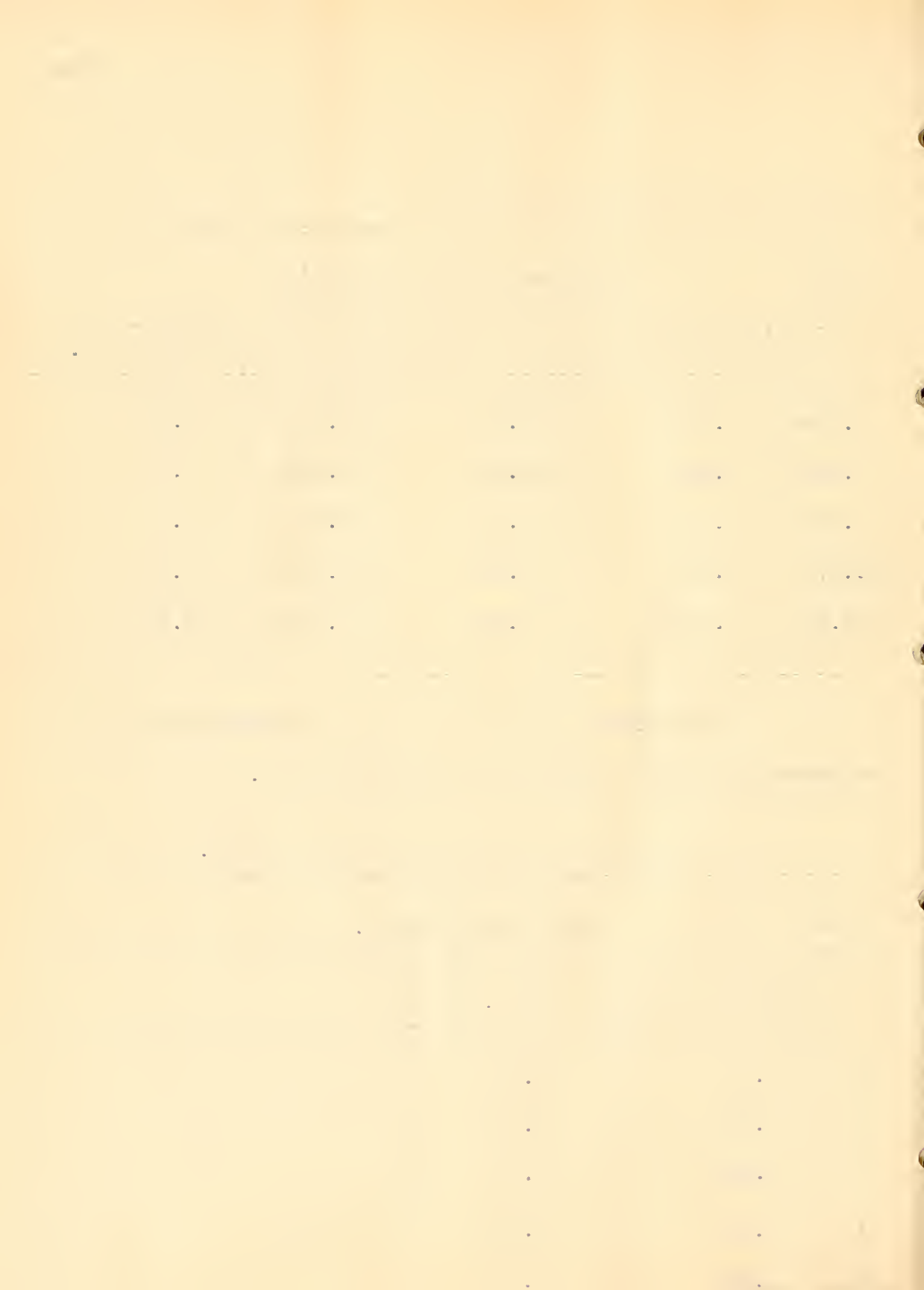
The minimum noticed in the case of praseodymium nitrate occurred here also, between the volumes 2 and 9.

The same calculated for even volumes.

LXXX

Neodymium Nitrate.

-v	Concentration	Molec. Dep.
2	0.5	11.80
4	0.25	11.87
6	0.166	11.70
10	0.100	11.90
20	0.05	11.24



XXXX Comparison. Neodymium Ammonium Nitrate.

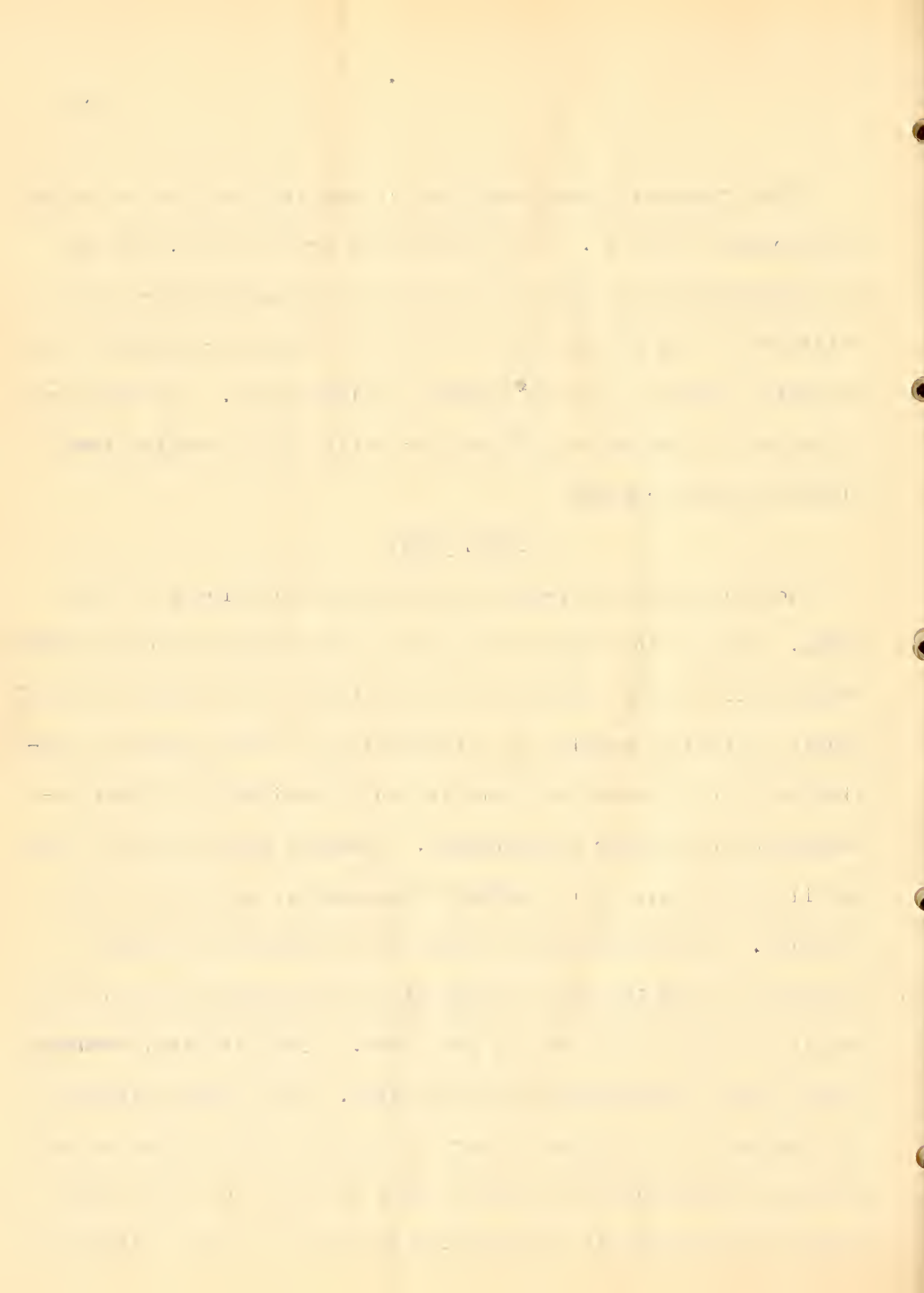
v	Δ NH_4NO_3	v	Δ $\text{Nd}(\text{NO}_3)_3$	Sum	Δ Double Salt	Dif.
1	6.27	2	11.80			
2	6.52	4	11.67			
3	6.71	6	11.70	18.41	18.10	0.31
5	6.96	10	11.90	18.36	18.36	0.50
10	7.26	20	12.24	19.50	18.54	0.96



The cryoscopic work here given is not as extensive as it had been hoped to make it. The indications from it, too, are not as satisfactory as those of the work on the conductivity of the solutions. The comparisons cannot be made with profit when the molecular depression curve shows a minimum point. The work was therefore not pushed and the results obtained are simply given without further comment.

CONCLUSION.

We may sum up the results of this investigation in a few words. We are led from the results of the study of the electrical conductivity of the solutions investigated to the belief that the double iodides of cadmium and strontium and of potassium and cadmium exist in concentrated solution to a considerable extent undecomposed into their constituents. They do not break down very readily but retain their compound character to moderately high dilutions. The same thing is found to be true of the double nitrates of ammonium with praseodymium and neodymium, and of the double cyanide of mercury and potassium. The nitrates, however, break down at comparatively low dilution. The double sulphates of ammonium with cadmium, copper, magnesium, iron, nickel as well as that of potassium and nickel appear not only to retain their undissociated state in concentrated but even in dilute solutions



they are not completely dissociated into their constituents.

A study of the conductivities of certain mixtures and double salts showed that the state of equilibrium is not necessarily always the same at the same concentration. While the double salt may not be completely dissociated at any given dilution,, the constituents do not combine to form the same amount of double salt when brought together at that dilution.

Cadmium sulphate, cadmium potassium iodide, praseodymium nitrate, ammonium praseodymium nitrate, neodymium nitrate are added to the list of those substances whose molecular depression of the freezing point of water does not increase ^{normally} with the dilution.

I had wished to undertake some electrolytic work with certain double salts to determine if possible the nature of the complex ion. Such an investigation is reserved for the future.

